Molecular Wires using (Oligo)pyrroles as Connecting Units – An Electron Transfer Study

*Ulrike Pfaff,[†] Alexander Hildebrandt,[†] Dieter Schaarschmidt,[†] Tobias Ruffer,[†] Paul J. Low[‡] and
Heinrich Lang^{*,†}*

[†] Institute of Chemistry, Inorganic Chemistry, Technische Universität Chemnitz, Faculty of Natural Sciences, D-09107 Chemnitz, Germany

[‡] School of Chemistry and Biochemistry, University of Western Australia, Crawley, Perth, WA, Australia

ABSTRACT

A series of (oligo)pyrroles featuring redox-active terminal ferrocenyl groups ($\text{Fc}_2\text{-(C}_4\text{H}_2\text{NPh)}_n$ (**4**, $n = 1$; **9**, $n = 2$; **16**, $n = 3$; **20**, $n = 4$)) has been prepared using a Negishi *C,C* cross-coupling reaction protocol. The bi-, ter- and quarterpyrrole wire moieties have been built up by *C,C* cross-coupling reactions of trimethyl silyl protected pyrrole units in the presence of $[\text{Pd}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{P}(\text{C}_4\text{H}_9)_2)(\mu\text{-Cl})_2]$ as precatalyst. The structural properties of the title compounds were investigated by spectroscopic means and single-crystal X-ray diffraction studies (**9**, **16** and **20**). The influence of the increasing number of *N*-phenyl pyrrole units on the electronic interaction between the iron centres was studied

using electrochemistry (cyclic (CV) and square wave voltammetry (SWV)) as well as spectro-electrochemistry (*in situ* UV-Vis/NIR spectroscopy). With exception of the diferrocenyl quarterpyrrole **20**, the application of $[N^mBu_4][B(C_6F_5)_4]$ as electrolyte allows the discrete oxidation of the ferrocenyl termini ($\Delta E^{o'} = 450$ mV (**4**), $\Delta E^{o'} = 320$ mV (**9**), $\Delta E^{o'} = 165$ mV (**16**)) in cyclic and square wave voltammograms. However, the iron centres of **20** were oxidized simultaneously, generating dicationic **20**²⁺. Additionally, one (**9**) or two (**16** and **20**) pyrrole-related well-defined reversible one-electron redox processes were observed. The cyclic voltammetry data reveal that the splitting of the ferrocene-based redox couples, $\Delta E^{o'}$, decreases with increasing oligo-pyrrole chain length and hence, the larger metal-metal distance. The trends in $\Delta E^{o'}$ with oligo-pyrrole structure also map to the electronic coupling between the ferrocene moieties as estimated by spectroelectrochemical UV-Vis/NIR measurements. Despite no direct metal-metal interaction in diferrocenyl quarterpyrrole **20**, a large absorption in the NIR region is observed arising from photo-induced charge transfer from the oligopyrrole backbone to the redox-active ferrocenyl termini. These charge transfer absorptions have also been found in the dicationic oxidation state of the mono-(**4**), bi- (**9**) and terpyrroles (**16**). Within this series of diferrocenyl(oligo)pyrroles this CT band is shifted bathochromically with increasing chain length of the backbone motif.

INTRODUCTION

During the last four decades significant interest has been focused on π -conjugated organic materials, which in addition to offering useful electronic and optical properties, for example, conductivity and electrochromism, are also finding application in the growing field of molecular electronics.¹⁻⁶

A convenient method through which to assess the effective delocalization of the π -electron density in these extended organic materials is to assess the mixed-valence characteristics of model complexes in which the target organic moiety serves as a bridging unit between two (or more) redox-active functionalities such as metallocenes^{7,8} and iron^{7,9} or ruthenium^{9,10} half-sandwich compounds. Due to the

excellent thermal stability and electrochemical reversibility of the ferrocene [Fe(II)/Fe(III)] redox couple, ferrocene is well-suited to such investigations.^{11,12} Many such ferrocene-based model systems with two redox-active termini have been described featuring a variety of π -conjugated organic bridges, *i.e.* diferrocenyl-polyenes,¹³ -arenes,¹⁴⁻¹⁷ -cumulenes¹⁸ and -oligo(phenylenevinylenes),¹⁹ and the redox-properties and electronic structures correlated with the wire-like behavior of the bridge. Of particular relevance to the present study are Sato's ter- to sexi-thiophene bridged bis-ferrocene complexes.^{20,21} These molecules were accessible by the Negishi cross-coupling of FcZnCl with the appropriate iodo-compounds. However, despite the intuitively appealing chemical structure, no direct interaction of the ferrocenyl units through the oligo(thiophene) chain was observed.

In a recent study we were able to show that the electron-rich pyrrole connecting unit is superior to the thiophene molecule in terms of promoting electronic interactions between ferrocenyl/ferrocenium termini.²² In that earlier work, a series of 2,5-diferrocenyl substituted furans, thiophenes and pyrroles were prepared and studied by electrochemical and spectroelectrochemical methods. The ferrocenyl moieties of these compounds showed two well-separated reversible one-electron redox processes. The separation of the redox potentials of 2,5-diferrocenyl-*N*-phenyl pyrrole ($\Delta E^{\circ'} = 450$ mV, supporting electrolyte: [NⁿBu₄][B(C₆F₅)₄]) was found to be much larger than those of 2,5-diferrocenyl thiophene ($\Delta E^{\circ'} = 260$ mV) under the same measurement conditions.^{16,22,23} Given the similar solvation, ion-pairing, inner and outer-sphere reorganisation energies, the $\Delta E^{\circ'}$ likely tracks reasonable well with the magnitude of 'electronic coupling' between the redox centers.²⁴ This prompted us to investigate model systems for molecular wires containing oligo(pyrrole) units, which might offer the possibility to observe electron transfer between the ferrocene-based redox centers through relatively long oligo-heterocyclic backbones.

We herein describe the synthesis of a series of diferrocenes bearing (oligo)pyrrole connecting units. (Spectro)electrochemical methods have been used to examine the effect of an increasing distance between the ferrocenyl moieties on the intermetallic communication of these complexes.

Synthesis and characterization

Scheme 1. Synthesis of oligopyrroles 2, 8, 14 and 18 ((i): 60 °C, 12 h, tetrahydrofuran, 0.25 mol% [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ-Cl)]₂, (NBS = *N*-bromosuccinimide)).

The introduction of the ferrocenyl substituents was realized by the convenient synthetic methodology shown in Scheme 2. Compound **1** and the fluorescent (oligo)pyrroles **7**, **14** and **18** were treated with two equivalents of *N*-bromosuccinimide resulting in the formation of dibrominated **2**, **8**, **15** and **19**.²⁵ Ferrocene was monolithiated according to the procedures reported by Müller-Westerhoff²⁷ followed by treatment with [ZnCl₂·2thf] to give FcZnCl, **3**. Subsequent reaction of **3** with 1/3rd equivalents of the dibromo compounds **2**, **8**, **15** and **19** under Negishi *C,C* cross-coupling conditions and appropriate work-up gave the (oligo)pyrroles **4**, **9**, **16** and **20** as orange solids in moderate to good yields (Experimental Section).

Scheme 2. Synthesis of diferrocenyl (oligo)pyrroles 4, 9, 16 and 20 ((i): 60 °C, 12 h, tetrahydrofuran, 0.25 mol% [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ-Cl)]₂, (NBS = *N*-bromosuccinimide)).

The diferrocenyl (oligo)pyrroles **4**, **9**, **16** and **20** are stable to air and moisture both in the solid state and in solution. They are poorly soluble in non-polar solvents such as *n*-hexane, diethyl ether and toluene but show good solubility in dichloromethane and tetrahydrofuran. Each of the compounds has been identified by NMR (¹H, ¹³C{¹H}) and IR spectroscopy as well as elemental analysis. In addition, high resolution ESI-TOF mass spectrometric measurements and single crystal X-ray diffraction studies (**9**, **16** and **20**) have been carried out. The electrochemical behavior of **4**, **9**, **16** and **20** was determined by cyclic voltammetry (= CV), square wave voltammetry (= SWV) and the redox products studied further by *in situ* UV-Vis/NIR spectroelectrochemical methods.

The IR spectra are less meaningful for the determination of the (oligo)pyrrolic chain length since they only show typical absorptions for the pyrrole moieties, the phenyl ring and the ferrocenyl units. The Me₃Si-protected oligopyrroles **10**, **11**, **13** and **17** show typical symmetric ($\nu_{s-\text{CH}_3}$) and asymmetric ($\nu_{as-\text{CH}_3}$) stretching vibrations below 3000 cm⁻¹ (Experimental Section). In contrast to the IR spectra, ¹H NMR spectra are more informative, with characteristic patterns of phenyl-pyrrole resonances clearly indicating the different number of pyrrole units. The terpyrroles **13**, **14**, **15** and **16** show a singlet for the protons of the middle pyrrole core between 5.72 to 6.36 ppm (Experimental Section). However, the bipyrroles **8** - **10** and quarterpyrroles **17**, **19** and **20** give two and four doublets corresponding to the CH protons of the pyrrole ring. Furthermore, these resonances are slightly shifted to higher field with increasing chain length. As expected the ferrocenyl units with their C₅H₅ and C₅H₄ cyclopentadienyl rings give rise to one singlet (C₅H₅) and two pseudotriplets (C₅H₄, AA'XX' spin system, $J = 1.80$ Hz) in each case (Experimental Section).

The structures of the diferrocenyl-substituted oligopyrroles **9**, **16** and **20** in the solid state have been determined by single crystal X-ray diffraction analysis. Suitable crystals were obtained by diffusion of methanol (**9** and **16**) or toluene (**20**) into a dichloromethane solution containing the respective compound at ambient temperature. Important bond distances (Å), bond angles (°) and torsion angles (°) are summarized in the captions of Figures 1 – 3, whilst crystal and structure refinement data are contained in the Experimental Section. The oligopyrroles crystallize in the triclinic space group *P*-1 (**9** and **20**) and in the monoclinic space group *P*2₁/*c* (**16**). In case of bipyrrrole **9**, the asymmetric unit contains two independent molecules. Each of the individual pyrrole heterocyclic moieties are essentially planar with rms deviations ranging from 0.0004–0.0066 Å (highest deviation observed for N1 (**16**) with 0.009(3) Å). Furthermore, electron delocalization within the individual pyrrole moieties can be inferred from the CC bond lengths, which fall between the distances of isolated single ($d_{C-C}^0 = 1.54$ Å²⁸) and double bonds ($d_{C=C}^0 = 1.34$ Å²⁸). The extent of delocalization can be expressed by calculating the

parameter τ as normalized quotient of the single and double bond length (Equation 1).²² Completely delocalized systems such as benzene evince a τ value of 1, while for localized systems τ approaches 0.²² For the oligopyrroles average τ values of 0.799 (**9**), 0.878 (**16**) and 0.803 (**20**) were obtained, which are in the same range as for unsubstituted pyrrole (0.830)²⁹ and 2,3,4,5-tetraferrocenyl-1-phenyl-1*H*-pyrrole (0.832)²³.

$$\tau = 1 + \frac{(d_{C-C}/d_{C=C}) - 1}{1 - (d_{C-C}^0/d_{C=C}^0)} \quad (1)^a$$

a) $d_{C-C}^0 = 1.54 \text{ \AA}$, $d_{C=C}^0 = 1.34 \text{ \AA}$, d_{C-C} = distance of the appropriate single bond, $d_{C=C}$ distance of the appropriate double bond.

Figure 1. ORTEP diagram (50 % probability level) of the molecular structure of **9** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°): average D–Fe = 1.647, N1–C14 = 1.383(3), C11–C12 = 1.368(3), C12–C13 = 1.396(3), C13–C14 = 1.370(3), C14–C21 = 1.462(3), C10–C11 = 1.464(3), C24–C31 = 1.467(3), N1–C15 = 1.436(3), N2–C25 = 1.423(3); C11–C12–C13 = 108.6(2), C11–N1–C14 = 108.7(2), N1–C14–C21 = 122.5(2), N1–C11–C12 = 107.1(2), average D–Fe–D = 178.3; N1–C14–C21–N2 = –155.8(2), C13–C14–C21–N2 = 33.9(4), C10–C11–N1–C15 = 1.0(4), C11–C12–C13–C14 = –0.3(3), N1–C14–C21–C22 = 36.1(4), (D = denotes the centroids of C₅H₄ and C₅H₅).

Figure 2. ORTEP diagram (50 % probability level) of the molecular structure of **16** with the atom numbering scheme. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°): average D–Fe = 1.666, N1–C33 = 1.426(7), N2–C39 = 1.450(7), N3–C45 = 1.442(6), N1–C11 = 1.394(6), N1–C14 = 1.406(6), C11–C12 = 1.373(7), C12–C13 = 1.403(7), C13–C14 = 1.381(7), C10–C11 = 1.468(7), C14–C15 = 1.444(7), C18–C19 = 1.428(7), C22–C23 = 1.447(7); average D–Fe–D = 177.5, C11–C12–C13 = 108.6(4), C11–N1–C14 = 108.8(4), N2–C18–C29 = 123.7(5), C18–N2–C39 = 121.4(4), C10–C11–N1 = 125.8(5); N1–C14–C15–N2 = 156.0(5), N2–C18–C19–N3 = 149.9(5), C10–C11–N1–C33 = 5.6(8), C11–C12–C13–C14 = 0.3(6), N1–C14–C15–C16 = -26.3(8), (D = denotes the centroids of C₅H₄ and C₅H₅).

In the solid state the oligopyrroles adopt a conformation in which the phenyl substituents point in different directions, in addition the pyrrole cores are not coplanar, as interplanar angles of 36.2(2), 34.0(2) (**9**), 27.2(3), 38.3(3) (**16**) and 83.1(1), 70.0(1), 77.7(2) ° (**20**) are observed. The CC bond distances between the ^cC₄N heterocycles are not affected by this torsion and are similar compared with related compounds.^{30,31} The ferrocenyl moieties in these compounds adopt an eclipsed conformation (4.9(2) Fe1, -3.2(3) Fe2, 6.0(3) Fe3, -9.3(3) Fe4 (**9**); 10.8(4) Fe1, 11.3(5) Fe2 (**16**); 4.2(3) Fe1, -1.1(8) ° Fe2 (**20**)) and are rotated by 21.1(1) (Fe1), 35.8(2) (Fe2) (**9**), 22.1(4) (Fe1), 27.9(3) (Fe2) (**16**), 9.8(3) (Fe1) and 12.5(5) ° (Fe2) (**20**) out of the plane of the adjacent pyrrole.

Figure 3. ORTEP diagram (50 % probability level) of the molecular structure of **20** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°): average D–Fe = 1.653, N1–C15 = 1.426(4), N2–C25 = 1.428(3), N3–C35 = 1.417(4), N4–C45 = 1.432(3), C6–C11 = 1.453(4), C11–N1 = 1.391(4), C11–C12 = 1.374(4), C12–C13 = 1.411(4), C13–C14 = 1.366(4), C14–N1 = 1.394(4), C14–C21 = 1.474(4), C24–C31 = 1.475(4), C34–C41 = 1.463(4), C44–C51 = 1.401(7); average D–Fe–D = 177.6, C11–C12–C13 = 108.1(3), C11–N1–C14 = 109.1(2), N2–C24–C31 = 123.1(2), N3–C34–C41 = 122.6(3), N4–C44–C51 = 129.9(5), C6–C11–N1 = 125.1(3); C31–C32–C33–C34 = 0.0(3), N1–C14–C21–N2 = 98.9(3), N2–C24–C31–N3 = 69.3(4), N3–C34–C41–N4 = 75.5(4), C7–C6–C11–N1 = –8.7(5), C35–N3–C34–C41 = –5.3(4), C43–C44–C51–C55 = 166.5(7), (D = denotes the centroids of C₅H₄ and C₅H₅).

Electrochemistry

The redox properties of oligopyrroles **7**, **13** and **17** and diferrocenyl-substituted (oligo)pyrroles **4**, **9**, **16** and **20** have been determined by cyclic voltammetry, square-wave voltammetry (Figures 4 and 5) and the redox products studied further by UV-Vis/NIR spectroscopy using spectroelectrochemical techniques (Figures 6, 7; Supporting Information Figures SI1, SI2, SI4 and SI5). Dichloromethane solutions containing the analyte (1.0 mmol·L^{–1}) and [NⁿBu₄][B(C₆F₅)₄] (0.1 mol·L^{–1})³² as supporting electrolyte were used for all measurements. The cyclic voltammetry measurements recorded at a scan rate of 100 mV·s^{–1} are summarized in Table 1. All redox potentials are referenced to the FcH/FcH⁺ redox couple ($E^{\circ'} = 0.00$ mV, FcH = Fe(η^5 -C₅H₅)₂).³³

Table 1. Cyclic voltammetry data (potentials *vs* FcH/FcH⁺), scan rate 100 mV·s⁻¹ at a glassy-carbon electrode of 1.0 mmol·L⁻¹ solutions of the analytes in dry dichloromethane containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte at 25 °C.

Compd.	$E_1^{o'} \text{ (mV)}^b$ ($\Delta E_p \text{ (mV)})^c$	$E_2^{o'} \text{ (mV)}^b$ ($\Delta E_p \text{ (mV)})^c$	$E_3^{o'} \text{ (mV)}^b$ ($\Delta E_p \text{ (mV)})^c$	$E_4^{o'} \text{ (mV)}^b$ ($\Delta E_p \text{ (mV)})^c$	$\Delta E^{o'} \text{ (mV)}^d$	K_C^e
4^a	-238 (68)	212 (75)	-	-	450	$4.08 \cdot 10^7$
9	-250 (74)	70 (74)	810 (74)	-	320	$2.58 \cdot 10^5$
16	-230 (68)	-65 (74)	480 (74)	1080 (72)	165	$6.17 \cdot 10^2$
20	-175 (90)	265 (66)	725 (63)	-	-	-

^aSee reference 23. ^b $E^{o'}$ = formal potential. ^c ΔE_p = difference between oxidation and reduction potential. ^d $\Delta E^{o'}$ = potential difference between the two ferrocenyl related redox processes. ^e K_C = comproportionation constant.

Figure 4 shows the cyclic and square wave voltammograms of diferrocenyl (oligo)pyrroles **4**, **9**, **16** and **20**. The ferrocenyl units of **4**, **9** and **16** are oxidized subsequently, while for **20** one reversible redox process was observed. The relatively high ΔE_p value (90 mV) and the larger $I_{c,p}$ and $I_{c,a}$ values of this redox event (Figure 4) indicate that two individual oxidation processes take place in a close potential range and hence are not resolved.³⁴ Due to the increasing chain length and therefore, the larger metal-metal distance, the redox splitting $\Delta E^{o'}$ between the ferrocenyl moieties decreases from 450 mV (**4**) to 320 mV (**9**) to 165 mV (**16**) (Table 1), and the corresponding comproportionation constants K_C ($R \cdot T \cdot \ln K_C = \Delta E^{o'} \cdot F$) have been determined (Table 1).³⁵ The larger K_C values are indicative for the high thermodynamic stability of the mixed-valent species with respect to disproportionation. Hence these molecules are suitable for spectroelectrochemical investigations (vide infra) as the chemical equilibrium (Equation 2) favors the mixed-valent form of the mono-oxidized compounds.

$$K_C = \frac{[M_1^n M_2^{n+1}]^2}{[M_1^n M_2^n][M_1^{n+1} M_2^{n+1}]} = e^{\frac{\Delta E^{o'} \cdot F}{RT}} \quad (2)$$

Figure 4. Voltammograms of dichloromethane solutions containing $1.0 \text{ mmol} \cdot \text{L}^{-1}$ of diferrocenyl (oligo)pyrrole **4**, **9**, **16** and **20** at 25°C . Supporting electrolyte $[\text{N}(\text{Bu})_4][\text{B}(\text{C}_6\text{F}_5)_4]$ ($0.1 \text{ mol} \cdot \text{L}^{-1}$). Left: Cyclic voltammograms (scan rate: $100 \text{ mV} \cdot \text{s}^{-1}$). Right: Square-wave voltammograms (scan rate: $1 \text{ mV} \cdot \text{s}^{-1}$).

In contrast to the oligo(pyrrole) bridged bis(ferrocene) complexes **4**, **9** and **16**, the analogous thiophene systems showed little or no redox splitting between the terminal ferrocenyl units ($\Delta E^{\circ'} = 260 \text{ mV}$ (2,5-diferrocenyl thiophene, dichloromethane, $[\text{N}(\text{Bu})_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as supporting electrolyte)²²; $\Delta E^{\circ'} = 130 \text{ mV}$ (5,5'-diferrocenyl-2,2'-bithiophene, dichloromethane, $[\text{N}(\text{Bu})_4][\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]$ as supporting electrolyte)^{16,36}). The group of Sato has synthesized related ter-, quarter-, quinque-, and sexithiophenes (substituted in position 3 with hexyl or methoxy groups to increase the solubility) with terminal ferrocenyl moieties to create model systems for molecular wires, but these complexes also exhibited little or no separation of the ferrocene-based redox processes.^{20,21} It seems likely that the larger redox splitting in the ferrocenyl-functionalized pyrroles **4**, **9** and **16** is caused by the smaller energy gap between the ferrocenyl moieties and the heterocyclic bridging moiety as well as the larger delocalization

of the pyrrole unit itself.²³ Therefore, the oligopyrroles may provide a more effective conduit for intermetallic charge transfer between the ferrocene units through the π -conjugated backbone.

In addition to the ferrocenyl-related redox events, at higher potential the oxidation of the pyrrole units could be observed for **9**, **16** and **20**. With increasing length of the pyrrolic π -system this oxidation process is shifted to cathodic potentials. This behavior is not unexpected as shown on the example of extended π -systems such as benzene, naphthalene and anthracene for which a similar potential shift could be observed.^{37,38} To verify the assignment of these additional redox events, electrochemical measurements of the non-ferrocenyl substituted oligopyrroles **7**, **13** and **17** have been carried out (Figure 5, Table 2).

Figure 5. Cyclic voltammograms (scan rate: $100 \text{ mV} \cdot \text{s}^{-1}$) of dichloromethane solutions containing $1.0 \text{ mmol} \cdot \text{L}^{-1}$ of oligopyrrole **7**, **13** and **17** at 25°C . Supporting electrolyte $[\text{N}(\text{}^n\text{Bu})_4][\text{B}(\text{C}_6\text{F}_5)_4]$ ($0.1 \text{ mol} \cdot \text{L}^{-1}$).

The first cycle in the voltammogram of bipyrrole **7** shows four irreversible oxidation processes, while further cycles give only an irreversible oxidation wave at 400 mV . This chemical behavior is not unexpected as upon oxidation a reactive radical cation is formed and polymerization as well as other

side reactions can occur easily through the 5 and 5' positions. In contrast, the cyclic voltammogram of the di(trimethylsilyl)-substituted quarterpyrrole **17** shows two well-separated reversible one-electron redox processes with a potential difference of $\Delta E^{\circ'} = 200$ mV, which is stable over more than 10 cycles. Extension of the oligo(pyrrole) π -system leads to the stabilization of the radical cation and suppresses the decomposition.

Table 2. Cyclic voltammetric data (potentials vs FcH/FcH⁺), scan rate 100 mV·s⁻¹ at a glassy-carbon electrode of 1.0 mmol·L⁻¹ solutions of the analytes in dry dichloromethane containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte at 25 °C.

Compd.	$E_1^{\circ'}$ (mV) ^a (ΔE_p (mV)) ^b	$E_2^{\circ'}$ (mV) ^a (ΔE_p (mV)) ^b	$E_3^{\circ'}$ (mV) ^a (ΔE_p (mV)) ^b	$E_4^{\circ'}$ (mV) ^a (ΔE_p (mV)) ^b	$\Delta E_1^{\circ'}$ (mV) ^c
7	280 (-)	400 (-)	930 (-)	1095 (-)	-
13	120 (-)	605 (-)	905 (-)	1190 (-)	-
17	5 (80)	205 (90)	-	-	200

^a $E^{\circ'}$ = formal potential. ^b ΔE_p = difference between oxidation and reduction potential. ^c $\Delta E^{\circ'}$ = potential difference between two redox processes.

A comparison with other unsubstituted oligopyrroles reported in the literature is difficult because the cyclic voltammetry data have been determined under different measurement conditions (acetonitrile and [NEt₄][BF₄] as supporting electrolyte). Hapiot *et al.* could detect one irreversible redox event for the bipyrrole ($E^{\circ'} = 600$ mV) and for the terpyrrole ($E^{\circ'} = 280$ mV), while for the quarterpyrrole two reversible redox processes ($E_1^{\circ'} = 160$ mV, $E_2^{\circ'} = 430$ mV) with a $\Delta E^{\circ'}$ value compatible to or measurements (170 mV) was observed.³⁹ Depending on the supporting electrolyte a different number of redox processes and varying potential differences was found. It could also be shown that the use of different electrolytes has a significant impact on the position and reversibility of the redox potentials, which has already been discussed in the literature.^{17,23,40,41} In comparison to the ferrocenyl-substituted analoga **9**, **16** and **20** the pyrrole-related oxidation is shifted to cathodic potentials. The ferrocenyl moieties of **9**, **16** and **20** are oxidized at lower potential than the appropriate oligopyrrole backbone,

therefore the thus formed ferrocenium units act as electron withdrawing substituents hindering the oxidation of the heterocycle.

Spectroelectrochemistry

The spectroelectrochemical studies were performed by stepwise increase of the potential (step heights: 25 mV, 50 mV or 100 mV) from -200 to 1000 mV vs Ag/AgCl in an OTTE (Optically Transparent Thin-Layer Electrochemistry) cell⁴² in dichloromethane solutions of **4**,²³ **9**, **16**, **17** and **20** (0.002 mol·L⁻¹) containing [NⁿBu₄][B(C₆F₅)₄] (0.1 mol·L⁻¹) as electrolyte at 25 °C. The stepwise increase of the potential allows, starting from the neutral (oligo)pyrroles **4**, **9**, **16**, **17** and **20**, the *in situ* generation of cationic **4**ⁿ⁺²³, **9**ⁿ⁺, **16**ⁿ⁺, **17**ⁿ⁺ and **20**⁽ⁿ⁺¹⁾⁺ (*n* = 1, 2) (Figure 6; Supporting Information Figures SI1, SI2, SI4 and SI5).

Figure 6. UV-Vis/NIR spectra of **9** at rising potentials vs Ag/AgCl: -200 to 350 mV (left top), 350 to 1000 mV (left bottom). Right: deconvolution of the NIR absorption at 350 mV (top) of *in situ* generated **9**⁺ and at 900 mV (bottom) of *in situ* generated **9**²⁺ using three Gaussian-shaped bands. Measurement conditions: 25 °C, dichloromethane, 0.1 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte.

The NIR data of **4** and its analysis has been published elsewhere.²³ Upon oxidation, diferrocenyl bipyrrrole **9** shows an increasing absorption in the NIR region at 2000 nm, which can be assigned to a CT (Charge Transfer) transition of the mixed-valent species **9**⁺. A further increase of the potential leads to the collapse of this absorption envelope and new bands at 1200 nm assigned to a LMCT (Ligand-to-Metal Charge Transfer) transition can be observed. To determine the physical parameters (wavenumber (ν_{max}), extinction (ϵ_{max}), Full-Width-at-Half-Maximum (= FWHM) ($\Delta\nu_{1/2}$)) of the charge transfer excitations in the NIR region, deconvolution assuming Gaussian shaped bands has been applied (Table 3).

Surprisingly upon enlargement of the pyrrolic chain the characteristics of the charge transfer absorptions change. Mixed valent **9**⁺ and **16**⁺ showed much more intense absorptions and a shift of the excitation maxima towards higher energy. Deconvolution of the charge transfer bands in **9**⁺ and **16**⁺ revealed that three bands contribute to the absorption in the NIR region for both compounds (Table 3, Figure 6, Figure SI1). None of these transitions showed typical characteristics^{43,44} of an IVCT (= Inter-Valence Charge Transfer) excitation and are much more intense than the IVCT band found in **4**²³. Therefore, it might be concluded that the classical two state model is not applicable to the elongated pyrrole systems (**9**, **16**), a more complex charge transfer behavior is observed. Especially for the terpyrrole **16**⁺ the characteristics of the CT absorption in the NIR resembles the one for dicationic **16**²⁺ pointing to a strong involvement of LMCT and inter-bridge-charge transfer interactions.

Table 3. NIR data of the diferrocenyl (oligo)pyrroles **4ⁿ⁺**, **9ⁿ⁺**, **16ⁿ⁺** and **20⁽ⁿ⁺¹⁾⁺** ($n = 1, 2$).^a

Compd.	transition	$\nu_{\max}$ (cm ⁻¹)	$\epsilon_{\max}$ (L·mol ⁻¹ ·cm ⁻¹)	$\Delta\nu_{1/2}$ (cm ⁻¹)
4⁺ ^b	LMCT	4256	1805	690
	IVCT	4820	4200	2369
4²⁺	LMCT	8500	190	900
	LMCT	9900	1500	3400
9⁺	CT	4800	6900	1700
	CT	5800	8200	2300
	CT	7800	2700	3850
9²⁺	LF ^c	4700	1950	1500
	CT	8200	11400	3900
	CT	7400	4000	2700
16⁺	CT	5400	10700	2100
	CT	6650	7450	2700
	CT	9100	3600	4050
16²⁺	CT	6200	11750	2800
	CT	8050	19900	3800
20²⁺	CT	5900	17600	2500
	CT	7800	21350	3600

^aIn dry dichloromethane containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte at 25 °C. ^bSee reference 23.

^cLigand field transition.

Due to the large metal-metal distance, mixed-valent **20⁺** showed no coupling between its redox-active moieties and is thermodynamically not stable under the applied conditions and hence the ferrocenyl termini in diferrocenyl quarterpyrrole are oxidized simultaneously. Therefore, the electronic character of the mixed-valent species cannot be determined by NIR spectroscopy. Nevertheless, **20²⁺** and **20³⁺** were *in situ* generated within the NIR measurement setup (Figure SI2) showing remarkably intense LMCT absorptions in the spectral range between 1250 and 1700 nm. To prove the character of these absorptions their solvatochromic behavior was studied using solvents with different polarities (dichloromethane ($\epsilon^\circ = 0.42$), tetrahydrofuran ($\epsilon^\circ = 0.45$), acetonitrile ($\epsilon^\circ = 0.65$)).⁴⁵ The thus observed solvatochromic shifts were negligible (< 100 nm) and proved the solvent independency of this charge transfer process (Figure SI3). A deconvolution of the NIR spectrum of **20²⁺** gives two large Gaussian-

shaped functions at 5900 cm^{-1} ($\Delta\nu_{1/2} = 2500\text{ cm}^{-1}$; $\epsilon_{\text{max}} = 17600\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and 7800 cm^{-1} ($\Delta\nu_{1/2} = 3600\text{ cm}^{-1}$; $\epsilon_{\text{max}} = 21350\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). Comparison with the spectroelectrochemical measurements of 4^{2+} , 9^{2+} and 16^{2+} showed that these compounds also exhibit weak to strong LMCT bands in a range between 1000 and 1740 nm. Extension of the oligo(pyrrole) π -system leads to a bathochromic shift of these LMCT transitions, while simultaneously increasing their intensity (Figure 7). With a decrease of the potential gap (Electrochemical Part Table 1, Figure 4) between the second ferrocenyl-related redox process and the first pyrrolic oxidation, the acceptor orbitals, within a ligand-to-metal charge transfer process, are raised, while the donor orbitals are lowered in energy. This results in a lower optical transition energy and thus a bathochromic shift. A comparable phenomenon has been described by Zhu and Wolf on the example of various ethynyl-ferrocenyl (oligo-)thiophenes.⁴⁶ They could show that a longer thiophene chain leads to a decreased energy difference between the ferrocenyl centered acceptor orbital and the thiophenic donor orbitals.⁴⁶ The different behavior of 4^{2+} in comparison to 9^{2+} , 16^{2+} and 20^{2+} again points to an involvement of inter-bridge charge transfer excitations for the elongated pyrroles, while 4^{2+} cannot possess such absorptions.

Figure 7. Bathochromic shift of the NIR spectra of 4^{2+} , 9^{2+} , 16^{2+} and 20^{2+} ($0.002\text{ mol}\cdot\text{L}^{-1}$ in dichloromethane) at $25\text{ }^{\circ}\text{C}$, supporting electrolyte $[\text{N}^{\text{B}}\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ ($0.1\text{ mol}\cdot\text{L}^{-1}$).

For comparison, the potential-depended UV-Vis/NIR spectra of 5,5'''-di(trimethylsilyl) quarterpyrrole (**17**) have been measured (Figure SI5). While no absorption could be found in a similar spectral region to the LMCT absorption, intense π - π^* absorptions below 1250 nm can be observed. Those sharp and intense bands could also be found in **9**²⁺ (624 nm), **16**²⁺ (696 nm) and **20**²⁺ (830 nm). For **4**, **9** and **16** (SI2) $^1A_{1g} \rightarrow ^1E_{1g}$ and $^1A_{1g} \rightarrow ^1E_{2g}$ *d-d* transitions of the ferrocenyl substituents⁴⁷ (465 and 650 nm (**4**), 450 and 670 nm (**9**), 520 and 810 nm (**16**)) can be detected in the UV-Vis region, which are shifted bathochromically compared to ferrocene (322 and 437 nm).⁴⁸ A bathochromic shift of the *d-d* transitions with increasing chain length of the (oligo)pyrroles can be seen indicating that less energy is necessary for these excitations.⁴⁹

CONCLUSION

A series of diferrocenyl-substituted (oligo)pyrroles **4**, **9**, **16** and **20** could be synthesized using palladium-catalyzed Negishi *C,C* cross-coupling reactions. Single crystal X-ray diffraction analysis of diferrocenyl bipyrrole (**9**), terpyrrole (**16**) and quarterpyrrole (**20**) show a decrease in coplanarity in the heterocyclic chain with growing number of pyrrole units. The redox behavior of the title compounds have been investigated by electrochemical methods such as cyclic voltammetry and square wave voltammetry. While the ferrocenyl moieties in quarterpyrrole **20** are oxidized simultaneously, the terminal units of pyrroles **4**, **9** and **16** show a redox splitting of 450 mV (**4**), 320 mV (**9**) and 165 mV (**16**) in the cyclic and square wave voltammograms. Additionally, one (**9**) or two (**16** and **20**) pyrrole-related well-defined reversible one-electron redox processes were observed. The metal-metal communication was further proven by UV-Vis/NIR spectroelectrochemical measurements, which showed absorptions in the NIR region. The characteristics of these absorptions have been analyzed by deconvolution calculations and solvatochromic experiments. While Mixed-valent compound **4**⁺ possess intense IVCT absorptions, the classical two state model seems not to be applicable to the longer

oligopyrroles (**9⁺**, **16⁺**). Diferrocenyl (oligo)pyrroles showed weak (**4**) to intense (**9**, **16** and **20**) CT absorptions in the dicationic oxidation state. In a good agreement with other published examples⁴⁶ those bands showed a bathochromic shift, when the chain length of the backbone is increased.

EXPERIMENTAL SECTION

General conditions. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, *n*-hexane and *n*-pentane were purified by distillation from sodium/benzophenone ketyl, toluene and diethyl ether were purified by distillation from sodium. Dichloromethane and *N,N*-dimethylformamide were purified by distillation from calcium hydride.

Reagents. ⁿBuLi (2.5 M solution in *n*-hexane), ^tBuLi (1.6 M solution in *n*-pentane), ferrocene, KO^tBu, *N*-phenylpyrrole, *N*-bromosuccinimide, trimethylsilyl chloride and tetra-*n*-butylammonium fluoride were purchased from commercial suppliers and used without further purification. 2-Bromo-*N*-phenylpyrrole (**1**), 2,5-dibromo-*N*-phenylpyrrole (**2**)²⁵ and [N(ⁿBu)₄][B(C₆F₅)₄]⁵⁰ were prepared according to published procedures. [ZnCl₂·2THF] was received by drying ZnCl₂ with thionyl dichloride and additional reaction with dry tetrahydrofuran. The palladium catalyst [P(^tC₄H₉)₂C(CH₃)₂CH₂Pd(μ -Cl)]₂ was synthesized according to Clark *et al.*²⁶

Instruments. ¹H NMR (500.3 MHz) and ¹³C{¹H} NMR (125.8 MHz) spectra were recorded with a Bruker Avance III 500 spectrometer operating at 298 K in the Fourier transform mode. Chemical shifts are reported in δ (parts per million) using undeuterated solvent residues as internal standard (chloroform-*d*₃: ¹H at 7.26 ppm and ¹³C{¹H} at 77.16 ppm; acetone-*d*₆: ¹H at 2.05 ppm and ¹³C{¹H} at 29.84 ppm, 206.26 ppm; dimethyl sulfoxide-*d*₆: ¹H at 2.50 ppm and ¹³C{¹H} at 39.52 ppm). Infrared spectra were recorded using a FT-Nicolet IR 200 equipment. The melting points of analytical pure samples (sealed off in nitrogen-purged capillaries) were determined using an Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed using a Thermo FLASH EA 1112 Series

instrument. Spectroelectrochemical measurements were carried out in an OTTLE cell⁴² from dichloromethane solutions containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte using a Varian Cary 5000 spectrometer. High-resolution mass spectra were performed using a micrOTOF QII Bruker Daltonics workstation.

Electrochemistry. Measurements on 1.0 mmol·L⁻¹ solutions of the analytes in dry air free dichloromethane containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte were conducted under a blanket of purified argon at 25 °C utilizing a Radiometer Voltalab 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 cm²), and an Ag/Ag⁺ (0.01 mol·L⁻¹ AgNO₃) reference electrode mounted on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with 1 μm and then 1/4 μm diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mol·L⁻¹ [AgNO₃] and 0.1 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)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 [NⁿBu₄][B(C₆F₅)₄] solution in dichloromethane.³² Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV. Experimentally potentials were referenced against an Ag/Ag⁺ reference electrode but results are presented referenced against ferrocene as an internal standard as required by IUPAC.³³ When decamethylferrocene was used as an internal standard, the experimentally measured potential was converted into *E* vs FcH/FcH⁺ by addition of -0.61 V.⁵¹ Data were then manipulated on a Microsoft Excel worksheet to set the formal redox potentials of the FcH/FcH⁺ couple to *E*^o = 0.0 V. The cyclic voltammograms, which are depicted, were taken after typical two scans and are considered to be steady state cyclic voltammograms, in which the signal pattern differs not from the initial sweep.

General procedure – Protection with trimethyl silyl group of 2 and 8. The dibromo (oligo)pyrroles **2** or **8** were dissolved in 50 mL of degassed tetrahydrofuran and treated with 1 eq of

n-butyllithium at -80 °C. After 1 h of stirring at this temperature the color of the solution changed from colorless to pale green (**10**) or deep purple (**11**). Then 1.1 eq of trimethyl silyl chloride was added in a single portion and the reaction mixture was slowly allowed to warm to ambient temperature and stirred overnight, whereby the color changed to yellow. After evaporation of all volatiles the crude product was purified by column chromatography (column size: 3 x 25 cm, alumina pretreated with triethyl amine, *n*-hexane as eluent). The 1st fraction contained the appropriate pure product and all volatiles were removed under reduced pressure.

Data for 2-Bromo-5-trimethylsilyl-*N*-phenyl pyrrole (10**).** 2,5-Dibromo-*N*-phenyl pyrrole (**2**) (8.29 g, 27.5 mmol), 1 eq of *n*-butyllithium (11.0 mL, 27.5 mmol) and 1.1 eq of trimethyl silyl chloride (3.83 mL, 30.0 mmol). Yield: 2.48 g (8.44 mmol, 31 % based on **2**); colorless, air-sensitive solid, soluble in dichloromethane. Anal. calcd for C₁₃H₁₆BrNSi (294.26 g/mol) [%]: C, 53.06; H, 5.48; N, 4.76; found: C, 53.00; H, 5.52; N, 4.65. Mp.: 51 °C. ¹H NMR [CDCl₃, ppm] δ: -0.04 (s, 9 H, SiC₃H₉), 6.32 (d, ³J_{H4-H3} = 3.69 Hz, 1 H, H-4), 6.48 (d, ³J_{H3-H4} = 3.69 Hz, 1 H, H-3), 7.28 (m, 2 H, C₆H₅/*o*-H), 7.46 (m, 3 H, C₆H₅). ¹³C{¹H} NMR [CDCl₃, ppm] δ: -0.29 (SiC₃H₉), 107.43 (C-2), 111.38 (C-4), 120.02 (C-3), 128.77 (C₆H₅), 128.91 (C₆H₅), 129.30 (C₆H₅), 136.85 (C_i-C₆H₅), 140.52 (C_i-C-SiC₃H₉). IR data [KBr, cm⁻¹] ν: 750 (s, δ_{o.o.p.} =C-H), 972 (s, δ_{C-N}), 1505 (s, ν_{C=C}), 1597 (m, ν_{C=C}), 2895 (w, ν_{s-CH₃}), 2954 (w, ν_{as-CH₃}), 3098 (w, ν_{=C-H}). HR-ESI-MS [*m/z*]: calcd for C₁₃H₁₆BrNSi: 295.0210, found: 295.0216 [M].

Data for 5-Bromo-5'-trimethylsilyl-*N,N'*-bisphenyl-2,2'-bipyrrole (11**).** 5,5'-Dibromo-*N,N'*-bisphenyl-2,2'-bipyrrole (**8**) (4.98 g, 11.3 mmol), 1 eq of *n*-butyllithium (4.53 mL, 11.3 mmol) and 1.1 eq of trimethyl silyl chloride (1.57 mL, 12.5 mmol). Yield: 4.12 g (9.46 mmol, 84 % based on **8**); colorless, air-sensitive solid, soluble in dichloromethane. Anal. calcd for C₂₃H₂₃BrN₂Si (435.43 g/mol) [%]: C, 63.44; H, 5.32; N, 6.43; found: C, 63.68; H, 5.48; N, 6.39. Mp.: 92 °C. ¹H NMR [CDCl₃, ppm] δ: -0.1

(s, 9 H, SiC₃H₉), 6.00 (d, $^3J_{\text{H4}'\text{-H3}'} = 3.81$ Hz, 1 H, H-4'), 6.03 (d, $^3J_{\text{H4-H3}} = 3.51$ Hz, 1 H, H-4), 6.18 (d, $^3J_{\text{H3}'\text{-H4}'} = 3.80$ Hz, 1 H, H-3'), 6.36 (d, $^3J_{\text{H3-H4}} = 3.62$ Hz, 1 H, H-3), 6.84 (m, 2 H, C₆H₅'), 6.89 (m, 2 H, C₆H₅), 7.21-7.36 (m, 6 H, C₆H₅/C₆H₅'). ¹³C{¹H} NMR [CDCl₃, ppm] δ : -0.05 (SiC₃H₉), 103.20 (C-5), 111.53 (C-3), 112.42 (C-3'), 112.70 (C-4'), 119.19 (C-4), 124.27 (C_i-C-2), 127.64 (C₆H₅), 127.78 (C₆H₅'), 128.38 (C₆H₅), 128.49 (C₆H₅'), 128.51 (C₆H₅), 128.63 (C₆H₅'), 130.36 (C_i-C-2'), 135.60 (C_i-C₆H₅'), 138.35 (C_i-C₆H₅), 141.24 (C_i-C-SiC₃H₉). IR data [KBr, cm⁻¹] ν : 751 (s, $\delta_{\text{o.o.p.}=\text{C-H}}$), 967 (m, $\delta_{\text{C-N}}$), 1497 (s, $\nu_{\text{C=C}}$), 1595 (m, $\nu_{\text{C=C}}$), 2889 (w, $\nu_{\text{s-CH}_3}$), 2948 (w, $\nu_{\text{as-CH}_3}$), 3100 (w, $\nu_{=\text{C-H}}$). HR-ESI-MS [m/z]: calcd for C₂₃H₂₃BrN₂Si: 437.0867, found: 437.0845 [M]⁺.

General procedure – Synthesis of bipyrrole and Me₃Si-protected oligopyrroles. To a solution of the monobromo (oligo)pyrroles **5** or **11** in 50 mL of degassed tetrahydrofuran was added dropwise *via* a syringe 1 eq of *n*-butyllithium (2.5 M in *n*-hexane) at -80 °C. The reaction mixture was stirred for 1 h. Then [ZnCl₂·2thf] (1 eq) was added in a single portion to generate *in situ* **6** or **12**. The reaction mixture was stirred for additional 30 min at 0 °C. Afterward, 0.25 mol% of [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ -Cl)]₂ and 1 eq of **5**, **10** or **11** were added in a single portion and the reaction solutions were stirred overnight at 60 °C. The crude product was worked-up by column chromatography (column size: 3 x 25 cm, alumina pretreated with triethyl amine). The 1st fraction contained the reactants **5** or **11**, while from the 2nd fraction the appropriate pure product could be obtained. All volatiles were removed under reduced pressure.

Data for *N,N'*-Bisphenyl-2,2'-bipyrrole (7**).** 2-Bromo-*N*-phenyl pyrrole (**5**) (2.95 g, 13.28 mmol), 1 eq of *n*-butyllithium (5.4 mL, 13.5 mmol), 1.0 eq of [ZnCl₂·2thf] (3.72 g, 13.5 mmol), 1 eq of 2-bromo-*N*-phenyl pyrrole (**5**) (2.95 g, 13.28 mmol) and 0.25 mol% of [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ -Cl)]₂ (22.8 mg). For column chromatography a *n*-hexane/diethyl ether mixture of ratio 6:1 (*v/v*) as eluent was used. Yield: 2.97 g (10.46 mmol, 77 % based on **5**); colorless, fluorescent solid, soluble in dichloromethane.

Anal. calcd for C₂₀H₁₆N₂ (284.35 g/mol) [%]: C, 84.48; H, 5.67; N, 9.85; found: C, 84.08; H, 5.92; N, 9.90. Mp.: 101 °C. ¹H NMR [CDCl₃, ppm] δ: 6.32 (pt, ³J_{H4-H3} = 3.58 Hz, ³J_{H4-H5} = 2.96 Hz, 2 H, H-4), 6.44 (dd, ⁴J_{H3-H5} = 1.84 Hz, ³J_{H3-H4} = 3.54 Hz, 2 H, H-3), 6.57-6.59 (m, 4 H, C₆H₅/*o*-H), 6.77 (dd, ⁴J_{H5-H3} = 1.80 Hz, ³J_{H5-H4} = 2.98 Hz, 2 H, H-5), 7.01 – 7.05 (m, 6 H, C₆H₅). ¹³C{¹H} NMR [CDCl₃, ppm] δ: 109.13 (C-4), 112.59 (C-3), 122.41 (C-5), 123.90 (C₆H₅), 125.18 (C_i-C-2), 125.57 (C₆H₅), 128.56 (C₆H₅), 140.30 (C_i-C₆H₅). IR data [KBr, cm⁻¹] ν: 718 (s, δ_{o.o.p.} =C-H), 1072 (m, ν_{C-N}), 1499 (s, ν_{C=C}), 1599 (m, ν_{C=C}), 3100 (w, ν_{=C-H}). HR-ESI-MS [*m/z*]: calcd for C₂₀H₁₆N₂: 566.2465, found: 566.2485 [M]₂.

Data for 5,5′′-Di-(trimethylsilyl)-*N,N′,N′′*-trisphenyl-2,2′:5′,2′′-terpyrrole (13). 5-Bromo-5′-trimethylsilyl-*N,N′*-bisphenyl-2,2′-bipyrrole (**11**) (1.66 g, 3.8 mmol), 1 eq of ⁿbutyllithium (1.53 mL, 3.8 mmol), 1.0 eq of [ZnCl₂·2thf] (1.07 g, 3.8 mmol), 1 eq of 2-bromo-5-trimethylsilyl-*N*-phenyl pyrrole (**10**) (1.12 g, 3.8 mmol) and 0.25 mol% of [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ-Cl)]₂ (6.53 mg). For column chromatography *n*-hexane was used as eluent. Yield: 0.91 g (1.6 mmol, 42 % based on **11**); colorless, fluorescent solid, soluble in dichloromethane. Anal. calcd for C₃₆H₃₉N₂Si₂ (569.89 g/mol) [%]: C, 75.87; H, 6.90; N, 7.37; found: C, 75.37; H, 7.26; N, 7.31. Mp.: 181 °C. ¹H NMR [CDCl₃, ppm] δ: - 0.12 (s, 18 H, SiC₃H₉), 6.02 (s, 2 H, H-3′/4′), 6.03 (d, ³J_{H4-H3/H4′′-H3′′} = 3.49 Hz, 2 H, H-4/4′), 6.28 (m, 2 H, C₆H₅′), 6.36 (d, ³J_{H3-H4/H3′′-H4′′} = 3.54 Hz, 2 H, H-3/3′), 6.62 (m, 4 H, C₆H₅/C₆H₅′), 6.96 (m, 2 H, C₆H₅′), 7.09 (m, 5 H, C₆H₅/C₆H₅′/C₆H₅′′) 7.18 (m, 2 H, C₆H₅/C₆H₅′). ¹³C{¹H} NMR [CDCl₃, ppm] δ: 0.01 (SiC₃H₉), 112.21 (C-3′/4′), 112.23 (C-3/3′), 119.19 (C-4/4′), 125.87 (C₆H₅′), 126.03 (C₆H₅/C₆H₅′), 127.03 (C₆H₅′), 127.15 (C₆H₅/C₆H₅′), 127.95 (C_i-C-2′/5′), 127.98 (C₆H₅′), 128.13 (C₆H₅/C₆H₅′), 130.96 (C_i-C-2/2′), 135.07 (C_i-C₆H₅/C_i-C₆H₅′), 138.87 (C_i-C₆H₅′), 141.24 (C_i-C-SiC₃H₉/C-SiC₃H₉′). IR data [KBr, cm⁻¹] ν: 756 (s, δ_{o.o.p.} =C-H), 1496 (s, ν_{C=C}), 1595 (m, ν_{C=C}), 2899 (w, ν_{s-CH3}), 2952 (w, ν_{as-CH3}), 3091 (w, ν_{=C-H}). HR-ESI-MS [*m/z*]: calcd for C₃₆H₃₉N₂Si₂: 570.2755, found: 570.2701 [M]⁺.

Data for 5,5'''-Di-(trimethylsilyl)-*N,N',N'',N'''*-tetrakisphenyl-2,2':5',2'':5'',2'''-quarter-pyrrole (17). 5-Bromo-5'-trimethylsilyl-*N,N'*-bisphenyl-2,2'-bipyrrole (**11**) (1.07 g, 2.47 mmol), 1 eq of *n*-butyllithium (1.0 mL, 2.47 mmol), 1.0 eq of [ZnCl₂·2thf] (0.69 g, 2.47 mmol), 1 eq of **11** (1.07 g, 2.47 mmol) and 0.25 mol% of [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ-Cl)]₂ (4.23 mg). For column chromatography a *n*-hexane/diethyl ether mixture of ratio 10:1 (v/v) was used as eluent. Yield: 0.99 g (1.4 mmol, 57 % based on **11**); colorless, fluorescent solid, soluble in dichloromethane. Anal. calcd for C₃₆H₃₉N₂Si₂ (711.06 g/mol) [%]: C, 77.70; H, 6.52; N, 7.88; found: C, 77.37; H, 6.70; N, 7.88. Mp.: 211 °C. ¹H NMR [CDCl₃, ppm] δ: -0.13 (s, 18 H, SiC₃H₉), 5.93 (d, ³J_{H4-H3/H4'''-H3'''} = 3.64 Hz, 2 H, H-4/4'''), 6.02 (d, ³J_{H3-H4/H3'''-H4'''} = 3.64 Hz, 2 H, H-3/3'''), 6.04 (d, ³J_{H3'-H4'/H4'''-H3'''} = 3.50 Hz, 2 H, H-3'/4'''), 6.07 (m, 4 H, C₆H₅/C₆H₅'''), 6.36 (d, ³J_{H4'-H3'/H3'''-H4'''} = 3.50 Hz, 2 H, H-4'/3'''), 6.58 (m, 4 H, C₆H₅'/C₆H₅'), 6.84 (m, 4 H, C₆H₅/C₆H₅'''), 6.98 (m, 2 H, C₆H₅/C₆H₅'''), 7.08 (m, 4 H, C₆H₅'/C₆H₅'), 7.18 (m, 2 H, C₆H₅'/C₆H₅'), 13C{¹H} NMR [CDCl₃, ppm] δ: -0.03 (SiC₃H₉), 111.98 (C-3'/4'''), 112.13 (C-4'/3'''), 112.26 (C-3/3'''), 119.16 (C-4/4'''), 125.53 (C₆H₅/C₆H₅'''), 125.92 (C_i-C-2'/5'), 126.11 (C_i-C-5'/2''), 126.75 (C₆H₅/C₆H₅'''), 127.01 (C₆H₅'/C₆H₅'), 127.68 (C₆H₅'/C₆H₅'), 127.99 (C₆H₅/C₆H₅'''), 128.05 (C₆H₅'/C₆H₅'), 130.94 (C_i-C-2/2'''), 135.11 (C_i-C₆H₅/C_i-C₆H₅'''), 138.52 (C_i-C₆H₅'/C₆H₅'), 141.20 (C_i-C-SiC₃H₉/C-SiC₃H₉'''). IR data [KBr, cm⁻¹] ν: 756 (s, δ_{o.o.p.} =C-H), 1497 (s, ν_{C=C}), 1596 (m, ν_{C=C}), 2893 (w, ν_{s-CH3}), 2952 (w, ν_{as-CH3}), 3097 (w, ν_{=C-H}). HR-ESI-MS [*m/z*]: calcd for C₄₆H₄₆N₄Si₂: 710.3275, found: 710.3256 [M].

General procedure – Deprotection of the oligopyrroles 13 and 17. The Me₃Si-protected oligopyrroles **13** and **17**, respectively, were dissolved in 20 mL of degassed tetrahydrofuran and 3 eq of tetra-*n*-butylammonium fluoride were added in a single portion at -40 °C. The reaction mixture was slowly warmed to ambient temperature and stirred for 2 d, whereby the colorless solution changed to pale blue. After evaporation of all volatiles the crude product was worked-up by filtration (column size: 1.5 x 10 cm, alumina pretreated with triethyl amine). For column chromatography a *n*-hexane/diethyl

ether mixture of ratio 10:1 (v/v) was used as eluent. The 1st fraction contained reactant **13** or **17**, while from the 2nd fraction the appropriate pure product could be isolated. All volatiles were removed under reduced pressure.

Data for *N,N',N''*-Trisphenyl-2,2':5',2''-terpyrrole (14**).** 5,5''-Di-(trimethylsilyl)-*N,N',N''*-trisphenyl-2,2':5',2''-terpyrrol (**13**) (0.72 g, 1.26 mmol) and 3 eq of tetra-*n*-butylammonium fluoride (1.19 g, 3.78 mmol). Yield: 0.51 g (1.19 mmol, 95 % based on **13**); colorless, fluorescent solid, soluble in dichloromethane. Anal. calcd for C₃₀H₂₃N₃ (425.52 g/mol) [%]: C, 84.68; H, 5.45; N, 9.87; found: C, 84.19; H, 5.77; N, 9.70. Mp.: 132 °C. ¹H NMR [CDCl₃, ppm] δ: 5.87 (m, ⁴*J*_{meta} = 1.23 Hz, 2 H, C₆H₅'), 6.19 (pt, ³*J*_{H4-H5/H4''-H5''} = 2.94 Hz, ³*J*_{H4-H3/H4''-H3''} = 3.61 Hz, 2 H, H-4/4''), 6.23 (dd, ⁴*J*_{H3-H5/H3''-H5''} = 1.82 Hz, ³*J*_{H3-H4/H3''-H4''} = 3.60 Hz, 2 H, H-3/3''), 6.36 (s, 2 H, H-3'/4'), 6.61 (m, 4 H, C₆H₅/C₆H₅''), 6.65 (m, 2 H, C₆H₅/C₆H₅''), 6.67 (dd, ⁴*J*_{H5-H3/H5''-H3''} = 1.82 Hz, ³*J*_{H5-H4/H5''-H4''} = 2.92 Hz, 2 H, H-5/5''), 6.82 (tt, ⁴*J*_{meta} = 1.21 Hz, 1 H, C₆H₅'), 7.04 (m, 6 H, C₆H₅/C₆H₅''/C₆H₅''). ¹³C{¹H} NMR [CDCl₃, ppm] δ: 108.82 (C-4/4''), 111.76 (C-3'/4'), 112.99 (C-3/3''), 122.27 (C-5/5''), 123.95 (C₆H₅/C₆H₅''), 125.08 (C₆H₅'), 125.23 (C₆H₅'), 125.65 (C₆H₅/C₆H₅''), 126.05 (C_i-C-2/2''), 126.31 (C₆H₅'), 127.50 (C_i-C-2'/5'), 128.56 (C₆H₅/C₆H₅''), 138.29 (C_i-C₆H₅'), 140.33 (C_i-C₆H₅/C_i-C₆H₅''). IR data [KBr, cm⁻¹] ν: 757 (s, δ_{o.o.p.} =C-H), 1499 (s, ν_{C=C}), 1599 (m, ν_{C=C}), 3055 (w, ν_{=C-H}). HR-ESI-MS [*m/z*]: calcd for C₃₀H₂₃N₃: 426.1965, found: 426.1962 [M]⁺.

Data for *N,N',N'',N'''*-Tetrakisphenyl-2,2':5',2'':5'',2'''-quarterpyrrole (18**).** 5,5'''-Di-(trimethylsilyl)-*N,N',N'',N'''*-tetrakisphenyl-2,2':5',2'':5'',2'''-quarterpyrrol (**17**) (0.686 g, 0.96 mmol) and 3 eq of tetra-*n*-butylammonium fluoride (0.913 g, 2.88 mmol). Yield: 0.545 g (0.96 mmol, 100 % based on **17**); colorless fluorescent solid, soluble in dichloromethane. Anal. calcd for C₄₀H₃₀N₄ (566.69 g/mol) [%]: C, 84.78; H, 5.34; N, 9.80; found: C, 84.60; H, 5.37; N, 9.80. Mp.: 177 °C. ¹H NMR [CDCl₃, ppm] δ: 5.97 (m, ³*J*_{ortho} = 7.83 Hz, 4 H, C₆H₅''/C₆H₅'''), 6.04 (d, ³*J*_{H3'-H4'/H4''-H3''} = 3.55 Hz, 2 H,

H-3'/4''), 6.18 (m, $^3J_{\text{H4-H5/H4}'''\text{-H5}'''} = 3.25$ Hz, 2 H, H-4/4''), 6.21 (m, $^3J_{\text{H5-H4/H5}'''\text{-H4}'''} = 3.25$ Hz, $^4J_{\text{H5-H3/H5}'''\text{-H3}'''} = 1.80$ Hz, 2 H, H-5/5''), 6.23 (d, $^3J_{\text{H4}'\text{-H3}''/\text{H3}'''\text{-H4}''} = 3.59$ Hz, 2 H, H-4'/3'), 6.56 (m, $^3J_{\text{ortho}} = 7.83$ Hz, 4 H, C₆H₅/C₆H₅''), 6.65 (m, $^4J_{\text{H3-H5/H3}'''\text{-H5}'''} = 1.82$ Hz, 2 H, H-3/3''), 6.73 (m, $^3J_{\text{ortho}} = 7.83$ Hz, 4 H, C₆H₅'/C₆H₅''), 6.88 (m, 2 H, C₆H₅'/C₆H₅''), 7.03 (m, $^3J_{\text{ortho}} = 7.83$ Hz, 4 H, C₆H₅/C₆H₅''), 7.08 (m, 2 H, C₆H₅/C₆H₅''). ¹³C{¹H} NMR [CDCl₃, ppm] δ: 108.83 (C-4/4''), 111.51 (C-3/3''), 112.14 (C-3'/4''), 112.92 (C-4/3''), 122.70 (C-5/5''), 123.90 (C₆H₅/C₆H₅''), 125.24 (C_i-2/2''), 125.28 (C₆H₅/C₆H₅''), 125.54 (C₆H₅'/C₆H₅''), 126.02 (C_i-C-5''/2''), 126.31 (C_i-C-5'/2''), 126.35 (C₆H₅'/C₆H₅''), 127.50 (C₆H₅'/C₆H₅''), 128.52 (C₆H₅/C₆H₅''), 138.25 (C_i-C₆H₅'/C_i-C₆H₅''), 140.34 (C_i-C₆H₅/C_i-C₆H₅''). IR data [KBr, cm⁻¹] ν: 769 (s, δ_{o.o.p.}=C-H), 1500 (s, ν_{C=C}), 1597 (m, ν_{C=C}), 3100 (w, ν_{C-H}). HR-ESI-MS [*m/z*]: calcd for C₄₀H₃₀N₄: 566.2453, found: 426.2465 [M].

General procedure – Synthesis of dibromo oligopyrroles 7, 14 and 18. According to a modified procedure from Gilow *et al.*²⁵ unsubstituted *N*-phenyl (oligo)pyrrole **7**, **14** and **18** were dissolved in 30 mL of degassed tetrahydrofuran and 2 eq of *N*-bromosuccinimide were added in a single portion at -78 °C. After 30 min of stirring at this temperature the solution was slowly warmed to ambient temperature and stirred for additional 2 h. Then the pink (**7**) or purple (**14** and **18**) reaction mixture was extracted three times with 20 mL of diethyl ether. The organic phase was washed three times with an aqueous Na₂CO₃ solution and dried over MgSO₄. The solvent was evaporated to dryness in oil-pump vacuum yielding a colorless precipitate.. The crude product was washed twice with cold *n*-pentane (0 °C) and finally dried in oil-pump vacuum.

Data for 5,5'-dibromo-*N,N'*-bisphenyl-2,2'-bipyrrole (8). *N,N'*-Bisphenyl-2,2'-bipyrrole (**3**) (2.36 g, 8.31mmol) and 2 eq of *N*-bromosuccinimide (2.96 g, 16.62 mmol). Yield: 2.88 g (6.54 mmol, 79 % based on **3**); colorless solid, soluble in dichloromethane. Anal. calcd for C₂₀H₁₄N₂Br₂ (442.15 g/mol) [%]: C, 54.33; H, 3.19; N, 6.34; found: C, 54.39; H, 3.36; N, 6.28. Mp.: 168.5 °C. ¹H NMR [CDCl₃,

ppm] δ : 6.05 (d, $^3J_{H_3-H_4} = 3.80$ Hz, 2 H, H-3), 6.19 (d, $^3J_{H_4-H_3} = 3.80$ Hz, 2 H, H-4), 6.79 (m, 4 H, C₆H₅), 7.22-7.27 (m, 6 H, C₆H₅). $^{13}\text{C}\{^1\text{H}\}$ NMR [CDCl₃, ppm] δ : 103.56 (C-5), 111.56 (C-3), 113.19 (C-4), 127.13 (C_i-C-2), 127.84 (C₆H₅), 128.38 (C₆H₅), 128.55 (C₆H₅), 137.90 (C_i-C₆H₅). IR data [KBr, cm⁻¹] ν : 755, 764 (s, $\delta_{\text{o.o.p.}=\text{C-H}}$), 1070 (m, $\nu_{\text{C-N}}$), 1496 (s, $\nu_{\text{C=C}}$), 1595 (m, $\nu_{\text{C=C}}$), 3032 (w, $\nu_{\text{C-H}}$). HR-ESI-MS [m/z]: calcd for C₂₀H₁₄N₂Br₂: 441.9499, found: 441.9499 [M].

Data for 5,5''-dibromo-*N,N',N''*-trisphenyl-2,2':5',2''-terpyrrole (15). *N,N',N''*-Trisphenyl-2,2':5',2''-terpyrrol (**14**) (0.43 g, 1.0 mmol) and 2 eq of *N*-bromosuccinimide (0.36 g, 2.0 mmol). Yield: 0.49 g (0.84 mmol, 84 % based on **14**); colorless solid, soluble in dichloromethane. Anal. calcd for C₃₀H₂₁N₃Br₂ (583.32 g/mol) [%]: C, 61.77; H, 3.63; N, 7.20; found: C, 61.55; H, 3.74; N, 6.89. Mp.: 181 °C. ^1H NMR [(CD₃)₂CO, ppm] δ : 5.94 (d, $^3J_{H_3-H_4/H_3''-H_4''} = 3.84$ Hz, 2 H, H-3/3''), 5.96 (s, 2 H, H-3'/4'), 6.17 (d, $^3J_{H_4-H_3/H_4''-H_3''} = 3.84$ Hz, 2 H, H-4/4''), 6.40 (m, 2 H, C₆H₅'), 6.72 (m, 4 H, C₆H₅/C₆H₅''), 7.09 (m, 2 H, C₆H₅'), 7.19 (m, 1 H, C₆H₅'), 7.27 (m, 4 H, C₆H₅/C₆H₅''), 7.34 (m, 2 H, C₆H₅/C₆H₅''). $^{13}\text{C}\{^1\text{H}\}$ NMR [(CD₃)₂CO, ppm] δ : 103.24 (C-5/5''), 112.19 (C-3'/4'), 113.34 (C-3/3''), 113.53 (C-4/4''), 126.63 (C_i-C-2/2''), 127.45 (C₆H₅'), 128.14 (C₆H₅/C₆H₅''), 128.44 (C₆H₅'), 128.60 (C₆H₅'), 129.01 (C_i-C-2'/5'), 129.03 (C₆H₅/C₆H₅''), 129.25 (C₆H₅/C₆H₅''), 138.69 (C_i-C₆H₅/C_i-C₆H₅''), 139.02 (C_i-C₆H₅'). IR data [KBr, cm⁻¹] ν : 757 (s, $\delta_{\text{o.o.p.}=\text{C-H}}$), 1497 (s, $\nu_{\text{C=C}}$), 1596 (m, $\nu_{\text{C=C}}$), 3059 (w, $\nu_{\text{C-H}}$). HR-ESI-MS [m/z]: calcd for C₃₀H₂₁N₃Br₂: 584.0157, found: 584.0087 [M]⁺.

Data for 5,5'''-dibromo-*N,N',N'',N'''*-tetrakisphenyl-2,2':5',2'':5'',2'''-quarterpyrrole (19). *N,N',N'',N'''*-Tetrakisphenyl-2,2':5',2'':5'',2'''-quarterpyrrol (**18**) (0.53 g, 0.94 mmol) and 2 eq of *N*-bromosuccinimide (0.33 g, 1.88 mmol). Yield: 0.62 g (0.86 mmol, 91 % based on **18**); colorless solid, soluble in dichloromethane. Anal. calcd for C₄₀H₂₈N₄Br₂ (724.49 g/mol) [%]: C, 66.31; H, 3.90; N, 7.73; found: C, 65.31; H, 3.98; N, 7.50. Mp.: 178 °C. ^1H NMR [CDCl₃, ppm] δ : 5.92 (d, $^3J_{H_4-H_3/H_4'''-H_3'''} = 3.61$ Hz, 2 H, H-4/4'''), 6.03-6.06 (m, 8 H, C₆H₅/C₆H₅'''/H-3/3'''/H-3'/4''), 6.18 (d, $^3J_{H_4'-H_3'/H_3'''-H_4''} =$

3.77 Hz, 2 H, H-4'/3''), 6.58 (m, 4 H, C₆H₅'/C₆H₅''), 6.85 (m, 4 H, C₆H₅/C₆H₅''), 7.00 (m, 2 H, C₆H₅/C₆H₅''), 7.12 (m, 4 H, C₆H₅'/C₆H₅''), 7.21 (m, 2 H, C₆H₅'/C₆H₅''). ¹³C{¹H} NMR [CDCl₃, ppm] δ: 102.88 (C-5/5''), 111.52 (C-3/3''), 112.02 (C-3'/4''), 112.50 (C-4'/3''), 112.78 (C-4/4''), 125.54 (C_i-C-2'/5''), 125.78 (C₆H₅/C₆H₅''), 126.23 (C_i-C-2/2''), 126.64 (C₆H₅/C₆H₅''), 127.32 (C₆H₅'/C₆H₅''), 127.67 (C_i-C-5'/2''), 127.85 (C₆H₅'/C₆H₅''), 128.14 (C₆H₅/C₆H₅'/C₆H₅''/C₆H₅''), 137.88 (C_i-C₆H₅/C₆H₅''), 138.14 (C_i-C₆H₅'/C₆H₅''). IR data [KBr, cm⁻¹] ν: 766 (s, δ_{o.o.p.} =C-H), 1497 (s, ν_{C=C}), 1596 (m, ν_{C=C}), 3042 (w, ν_{C-H}). HR-ESI-MS [*m/z*]: calcd for C₄₀H₂₈N₄Br₂: 724.0694, found: 724.0659 [M].

General procedure – Synthesis of diferrocenyl oligopyrroles 8, 15 and 19. Ferrocene and KO^tBu (0.125 eq) were dissolved in 20 mL of tetrahydrofuran and the solution was cooled to -80 °C. ^tButyllithium (2 eq, 1.6 M in *n*-pentane) was added dropwise *via* a syringe and the solution was stirred for 1 h. Then [ZnCl₂·2thf] (1 eq) was added in a single portion. The reaction mixture was stirred for additional 30 min at 0 °C. Afterward, 0.25 mol% of [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ-Cl)]₂ and 1/3 eq of the bromo oligopyrroles **8**, **15** or **19** were added in a single portion and the reaction solutions were stirred overnight at 60 °C. The crude product was worked-up by column chromatography (column size: 1.5 x 10 cm, alumina pretreated with triethyl amine). The 1st fraction contained ferrocene, while from the 2nd fraction **9**, **16** or **20** could be isolated. All volatiles were removed under reduced pressure.

Data for 5,5'-diferrocenyl-*N,N'*-bisphenyl-2,2'-bipyrrole (9). Ferrocene (0.35 g, 1.89 mmol), 0.125 eq of KO^tBu (27 mg, 0.24 mmol), 2 eq of ^tbutyllithium (2.35 mL, 3.78 mmol), 1.0 eq of [ZnCl₂·2thf] (527 mg, 1.89 mmol), 1/3 eq of 5,5'-dibromo-*N,N'*-bisphenyl-2,2'-bipyrrol (**8**) (0.28 g, 0.63 mmol) and 0.25 mol% of [Pd(CH₂C(CH₃)₂P(C₄H₉)₂)(μ-Cl)]₂ (2.14 mg). As eluent for column chromatography a *n*-hexane/diethyl ether mixture of ratio 10:1 (v/v) was used. Yield: 0.3 g (0.45 mmol, 73 % based on **8**); pale orange solid, soluble in dichloromethane. Anal. calcd for C₄₀H₃₂N₂Fe₂ (652.38

g/mol) [%]: C, 73.64; H, 4.94; N, 4.29; found: C, 73.61; H, 5.40; N, 4.10. Mp.: 221 °C. ^1H NMR [CDCl_3 , ppm] δ : 3.84 (pt, $J_{\text{HH}} = 1.90$ Hz, 4 H, C_5H_4), 3.97 (s, 10 H, C_5H_5), 3.98 (pt, $J_{\text{HH}} = 1.90$ Hz, 4 H, C_5H_4), 6.03 (d, $^3J_{\text{H3-H4}} = 3.67$ Hz, 2 H, H-3), 6.30 (d, $^3J_{\text{H4-H3}} = 3.67$ Hz, 2 H, H-4), 6.85 (m, 4 H, $\text{C}_6\text{H}_5/o\text{-H}$), 7.22-7.25 (m, 6 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR [CDCl_3 , ppm] δ : 67.51 (C_5H_4), 67.56 (C_5H_4), 69.60 (C_5H_5), 79.26 ($\text{C}_i\text{-C}_5\text{H}_4$), 108.09 (C-4), 112.47 (C-3), 126.65 (C-5), 127.41 (C_6H_5), 128.27 (C_6H_5), 129.08 (C_6H_5), 131.85 ($\text{C}_i\text{-C-2}$), 139.41 ($\text{C}_i\text{-C}_6\text{H}_5$). IR data [KBr , cm^{-1}] ν : 775 (s, $\delta_{\text{o.o.p.}} = \text{C-H}$), 1105 (m, $\nu_{\text{C-N}}$), 1500 (s, $\nu_{\text{C=C}}$), 1590 (m, $\nu_{\text{C=C}}$), 3080 (w, $\nu_{\text{C-H}}$). HR-ESI-MS [m/z]: calcd for $\text{C}_{40}\text{H}_{32}\text{N}_2\text{Fe}_2$: 652.1260, found: 652.1263 [M].

Data for 5,5''-diferrocenyl- N,N',N'' -trisphenyl-2,2':5',2''-terpyrrole (16). Ferrocene (383 mg, 2.06 mmol), 0.125 eq of KO^tBu (29 mg, 0.26 mmol), 2 eq of t -butyllithium (2.57 mL, 4.12 mmol), 1.0 eq of $[\text{ZnCl}_2 \cdot 2\text{thf}]$ (577 mg, 2.06 mmol), 1/3 eq of 5,5''-dibromo- N,N',N'' -trisphenyl-2,2':5',2''-terpyrrol (**15**) (0.40 g, 0.69 mmol) and 0.25 mol% of $[\text{Pd}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{P}(\text{C}_4\text{H}_9)_2)(\mu\text{-Cl})_2]$ (2.35 mg). As eluent for column chromatography a n -hexane/diethyl ether mixture of ratio 2:1 (v/v) was used. Yield: 0.3 g (0.38 mmol, 55 % based on **15**); orange solid, soluble in dichloromethane. Anal. calcd for $\text{C}_{50}\text{H}_{39}\text{N}_3\text{Fe}_2 \cdot 0.85\text{Et}_2\text{O}$ (856.55 g/mol) [%]: C, 74.87; H, 5.59; N, 4.90; found: C, 74.56; H, 5.30; N, 4.90. Mp.: 185 °C (decomp.). ^1H NMR [$(\text{CD}_3)_2\text{SO}$, ppm] δ : 3.78 (pt, $J_{\text{HH}} = 1.88$ Hz, 4 H, C_5H_4), 3.92 (s, 10 H, C_5H_5), 4.01 (pt, $J_{\text{HH}} = 1.88$ Hz, 4 H, C_5H_4), 5.70 (d, $^3J_{\text{HH}} = 3.65$ Hz, 2 H, H-3/3''), 5.72 (s, 2 H, H-3'/4'), 6.25 (d, $^3J_{\text{HH}} = 3.65$ Hz, 2 H, H-4/4''), 6.70 (m, 2 H, $\text{C}_6\text{H}_5'/o\text{-H}$), 6.82 (m, 4 H, $\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''/o\text{-H}$), 7.21 (m, 3 H, $\text{C}_6\text{H}_5'$), 7.32 (m, 4 H, $\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''/m\text{-H}$), 7.39 (m, 2 H, $\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''/p\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR [$(\text{CD}_3)_2\text{SO}$, ppm] δ : 66.28 (C_5H_4), 67.29 (C_5H_4), 69.20 (C_5H_5), 78.42 ($\text{C}_i\text{-C}_5\text{H}_4$), 107.67 (C_4N), 111.34 (C_4N), 111.64 (C_4N), 125.48 ($\text{C}_i\text{-C-5/5''}$), 126.12 ($\text{C}_i\text{-C-2/2''}$), 126.59 ($\text{C}_6\text{H}_5'$), 127.70 ($\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 127.86 ($\text{C}_6\text{H}_5'$), 127.98 ($\text{C}_6\text{H}_5'$), 128.34 ($\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 128.83 ($\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 131.25 ($\text{C}_i\text{-C-2'/5'}$), 138.43 ($\text{C}_i\text{-C}_6\text{H}_5'$), 138.59 ($\text{C}_i\text{-C}_6\text{H}_5/\text{C}_i\text{-C}_6\text{H}_5''$). IR data [KBr , cm^{-1}] ν : 768 (s, $\delta_{\text{o.o.p.}}$).

=C-H), 1497 (s, $\nu_{\text{C}=\text{C}}$), 1596 (m, $\nu_{\text{C}=\text{C}}$), 3055, 3098 (w, $\nu_{\text{C-H}}$). HR-ESI-MS [m/z]: calcd for $\text{C}_{50}\text{H}_{39}\text{N}_3\text{Fe}_2$: 794.1918, found: 794.1815 [M]⁺.

Data for 5,5'''-diferrocenyl-*N,N',N'',N'''*-tetrakisphenyl-2,2':5',2'':5'',2'''-quarterpyrrole (20).

Ferrocene (466 mg, 2.5 mmol), 0.125 eq of KO^tBu (35 mg, 0.31 mmol), 2 eq of ^tbutyllithium (3.13 mL, 5.0 mmol), 1.0 eq of $[\text{ZnCl}_2 \cdot 2\text{thf}]$ (0.70 g, 2.5 mmol), 1/3 eq of 5,5'''-dibromo-*N,N',N'',N'''*-tetrakisphenyl-2,2':5',2'':5'',2'''-quarterpyrrol (**19**) (0.60 g, 0.84 mmol) and 0.25 mol% of $[\text{Pd}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{P}(\text{C}_4\text{H}_9)_2)(\mu\text{-Cl})_2]$ (4.30 mg). For column chromatography a *n*-hexane/dichloromethane mixture of ratio 5:1 (v/v) was used as eluent. Yield: 0.65 g (0.69 mmol, 83 % based on **19**); orange solid, soluble in dichloromethane. Anal. calcd for $\text{C}_{40}\text{H}_{46}\text{N}_4\text{Fe}_2$ (934.24 g/mol) [%]: C, 77.10; H, 4.96; N, 5.99; found: C, 77.03; H, 5.36; N, 5.83. Mp.: 227 °C (decomp.). ¹H NMR [CDCl_3 , ppm] δ : 3.80 (pt, $J_{\text{HH}} = 1.89$ Hz, 4 H, C_5H_4), 3.95 (s, 10 H, C_5H_5), 3.97 (pt, $J_{\text{HH}} = 1.90$ Hz, 4 H, C_5H_4), 5.95 (d, $^3J_{\text{HH}} = 3.58$ Hz, 2 H, H-4/4'''), 6.03 (d, $^3J_{\text{HH}} = 3.67$ Hz, 2 H, H-3'/4''), 6.06 (d, $^3J_{\text{HH}} = 3.56$ Hz, 2 H, H-3/3''), 6.14 (m, 4 H, $\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 6.30 (d, $^3J_{\text{HH}} = 3.67$ Hz, 2 H, H-4'/3''), 6.55 (m, 4 H, $\text{C}_6\text{H}_5'/\text{C}_6\text{H}_5''$), 6.86 (m, 4 H, $\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 6.97 (m, 2 H, $\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 7.10 (m, 4 H, $\text{C}_6\text{H}_5'/\text{C}_6\text{H}_5''$), 7.21 (m, 2 H, $\text{C}_6\text{H}_5'/\text{C}_6\text{H}_5''$). ¹³C{¹H} NMR [CDCl_3 , ppm] δ : 67.47 (C_5H_4), 67.53 (C_5H_4), 69.60 (C_5H_5), 79.09 ($\text{C}_i\text{-C}_5\text{H}_4$), 108.09 (C_4N), 111.77 (C_4N), 112.32 (C_4N), 112.41 (C_4N), 125.47 ($\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 126.07 ($\text{C}_i\text{-C-}2/2''$), 126.10 ($\text{C}_i\text{-C-}2'/5''$), 126.53 ($\text{C}_i\text{-C-}5/5''$), 126.77 ($\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 127.04 ($\text{C}_6\text{H}_5'/\text{C}_6\text{H}_5''$), 127.65 ($\text{C}_6\text{H}_5'/\text{C}_6\text{H}_5''$), 127.97 ($\text{C}_6\text{H}_5/\text{C}_6\text{H}_5''$), 128.68 ($\text{C}_6\text{H}_5'/\text{C}_6\text{H}_5''$), 131.09 ($\text{C}_i\text{-C-}5'/2''$), 138.55 ($\text{C}_i\text{-C}_6\text{H}_5/\text{C}_i\text{-C}_6\text{H}_5''$), 138.98 ($\text{C}_i\text{-C}_6\text{H}_5'/\text{C}_i\text{-C}_6\text{H}_5''$). IR data [KBr , cm^{-1}] ν : 769 (s, $\delta_{\text{o.o.p.}}$ =C-H), 1498 (s, $\nu_{\text{C}=\text{C}}$), 1596 (m, $\nu_{\text{C}=\text{C}}$), 3055, 3091 (w, $\nu_{\text{C-H}}$). HR-ESI-MS [m/z]: calcd for $\text{C}_{60}\text{H}_{46}\text{N}_4\text{Fe}_2$: 934.2419, found: 934.2410 [M].

Single crystal X-ray diffraction analysis. Data were collected on an Oxford Gemini S diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) (compound **9**) or Cu K α radiation (1.54184 Å) (**16**, **20**). The molecular structures were solved by direct methods using SHELXS-97⁵² and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.⁵³ All non-hydrogen atoms

were refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions.

Crystal data for 9. Single crystals of **9** were obtained by diffusion of methanol into a dichloromethane solution containing **9** at 25 °C. $C_{40}H_{32}Fe_2N_2$, $M_r = 652.38 \text{ g}\cdot\text{mol}^{-1}$, crystal dimensions 0.15 x 0.12 x 0.08 mm, triclinic, $P\bar{1}$, $\lambda = 0.71073 \text{ \AA}$, $a = 12.8550(5) \text{ \AA}$, $b = 16.1262(4) \text{ \AA}$, $c = 16.9337(6) \text{ \AA}$, $\alpha = 112.931(3)^\circ$, $\beta = 105.841(3)^\circ$, $\gamma = 97.547(3)^\circ$, $V = 2996.19(17) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.446 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 1.001 \text{ mm}^{-1}$, $T = 110 \text{ K}$, $\Theta \text{ range} = 2.90 - 26.00^\circ$, reflections collected 27603, independent 11692, $R_1 = 0.0387$, $wR_2 = 0.0772 [I \geq 2\sigma(I)]$.

Crystal data for 16·0. MeOH. Single crystals of **16·0.5 MeOH** were obtained by diffusion of methanol into a dichloromethane solution containing **16** at 25 °C. $C_{50.5}H_{41}Fe_2N_3O_{0.5}$, $M_r = 809.56 \text{ g}\cdot\text{mol}^{-1}$, crystal dimensions 0.40 x 0.10 x 0.01 mm, monoclinic, $P2_1/c$, $\lambda = 1.54184 \text{ \AA}$, $a = 16.2608(7) \text{ \AA}$, $b = 23.0890(11) \text{ \AA}$, $c = 10.5432(4) \text{ \AA}$, $\beta = 98.853(4)^\circ$, $V = 3910.9(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.375 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 6.263 \text{ mm}^{-1}$, $T = 115 \text{ K}$, $\Theta \text{ range} = 3.35 - 63.99^\circ$, reflections collected 12791, independent 6392, $R_1 = 0.0598$, $wR_2 = 0.1297 [I \geq 2\sigma(I)]$.

Crystal data for 20. Single crystals of **20** were obtained by diffusion of toluene into a dichloromethane solution containing **20** at 25 °C. $C_{60}H_{46}Fe_2N_4$, $M_r = 934.71 \text{ g}\cdot\text{mol}^{-1}$, crystal dimensions 0.36 x 0.18 x 0.12 mm, triclinic, $P\bar{1}$, $\lambda = 1.54184 \text{ \AA}$, $a = 7.2632(3) \text{ \AA}$, $b = 15.1417(6) \text{ \AA}$, $c = 20.1823(8) \text{ \AA}$, $\alpha = 76.704(3)^\circ$, $\beta = 87.070(3)^\circ$, $\gamma = 79.227(3)^\circ$, $V = 2188.19(15) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.419 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 5.677 \text{ mm}^{-1}$, $T = 115 \text{ K}$, $\Theta \text{ range} = 3.05 - 62.93^\circ$, reflections collected 12059, independent 6903, $R_1 = 0.0455$, $wR_2 = 0.1122 [I \geq 2\sigma(I)]$.

AUTHOR INFORMATION

*Corresponding author. E-mail: heinrich.lang@chemie.tu-chemnitz.de; phone: +49 (0)371-531-21210; fax.: +49 (0)371-531-21219.

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Molecular Wires using (Oligo)pyrroles as Connecting Units – An Electron Transfer Study

*Ulrike Pfaff, Alexander Hildebrandt, Dieter Schaarschmidt, Tobias Rüffer, Paul J. Low and Heinrich
Lang*

A series of diferrocenyl (oligo)pyrroles have been prepared using the Negishi *C,C* cross-coupling protocol. In the electrochemical measurements a separate oxidation of the ferrocenyls (one to three pyrrole units) and additional oxidation processes for the pyrrole units could be observed. The NIR measurements confirm electronic communication between the ferrocenyl termini in the corresponding mixed-valent systems of the (oligo)pyrroles up to three pyrrole units.

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