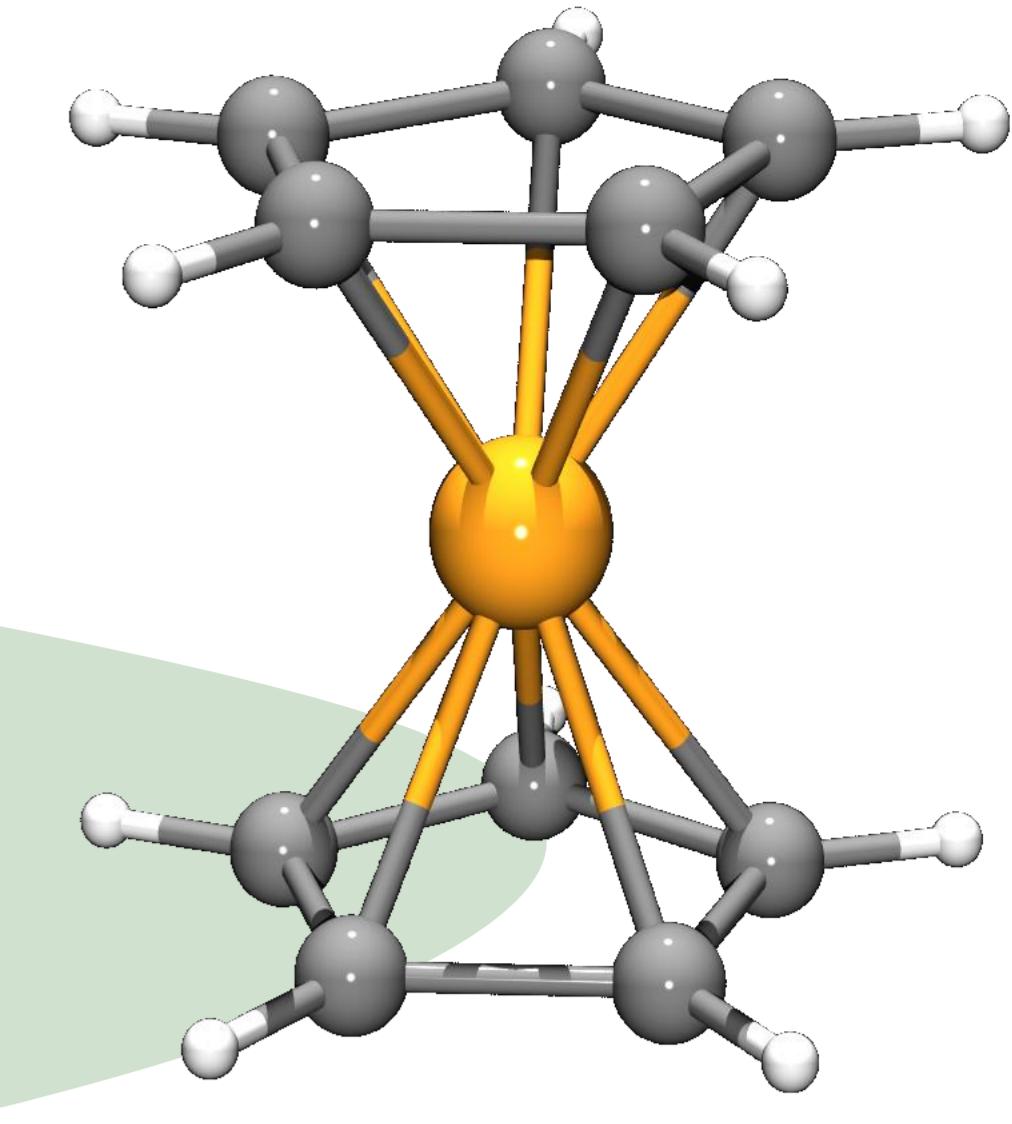


# Diferrocenyl (Oligo)pyrroles Influencing Electronic Intercommunication

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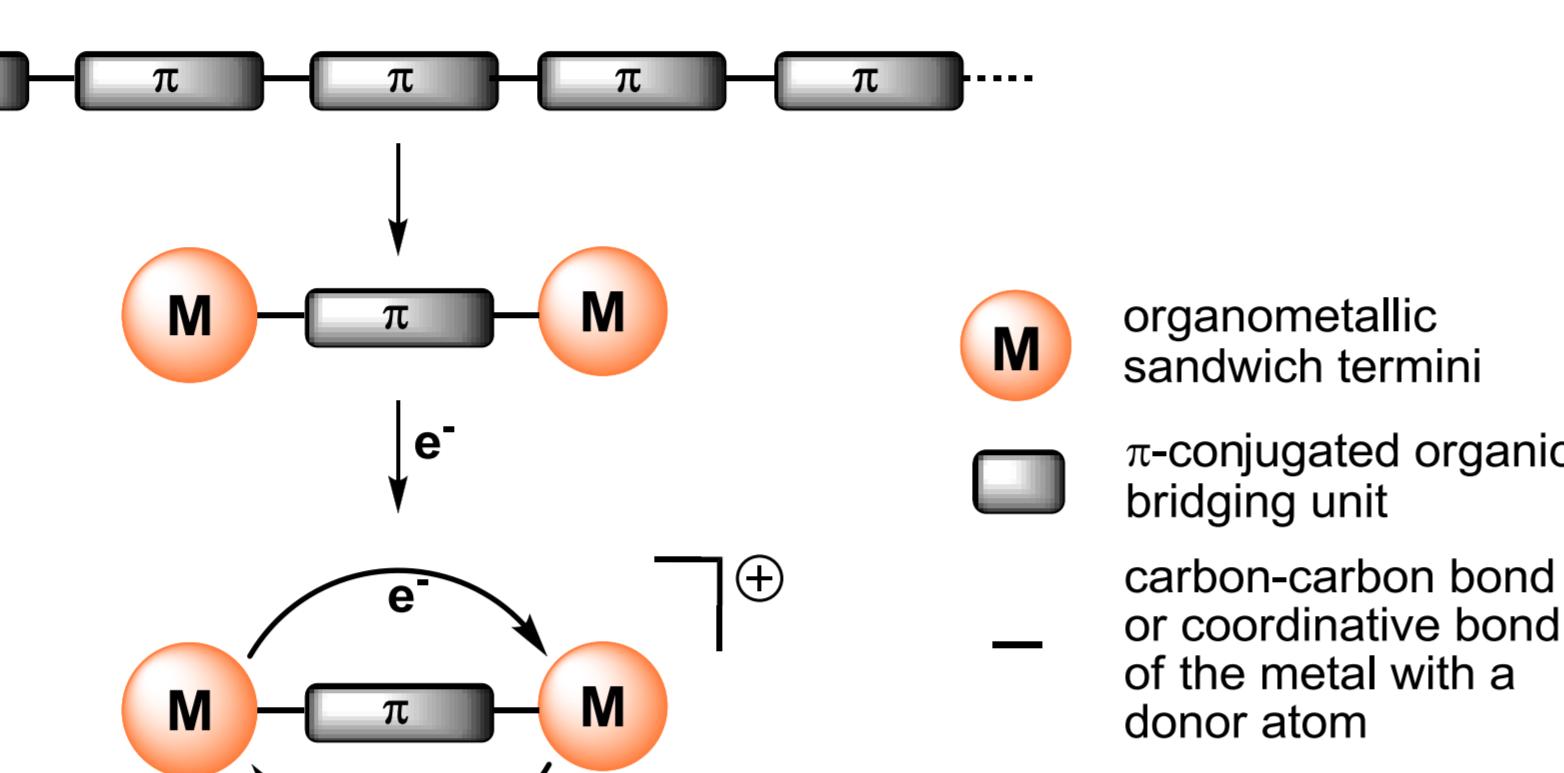
## Introduction

During recent years the development of compounds with redox-active metal centres has attracted considerable attention since they can be applied as new materials with novel chemical, physical and/or electronic properties in the field of material science.<sup>[1]</sup> Therefore, homo- and heterodinuclear complexes connected by  $\pi$ -conjugated organic

units were designed as simple models for molecular wires<sup>[2]</sup> and novel electro-active materials.<sup>[3]</sup> Complexes with ferrocenyls as redox-active termini are extensively explored<sup>[4]</sup> focusing on the electrochemical behavior and on electron transfer processes.

## Motivation

To investigate electron transfer in molecular wires, it is useful to study molecules with small bridging units between ferrocenyl-termini. Recently, we reported about the synthesis and characterization of a series of 2,5-di- and 2,3,4,5-tetraferrocenyl-substituted furans, thiophenes and pyrroles.<sup>[5]</sup>



In continuation of our work on ferrocenyl-functionalized heteroaromatics, we here present the design and (spectro-)electrochemical behavior of ferrocenyl-substituted oligopyrroles.

## Electrochemistry

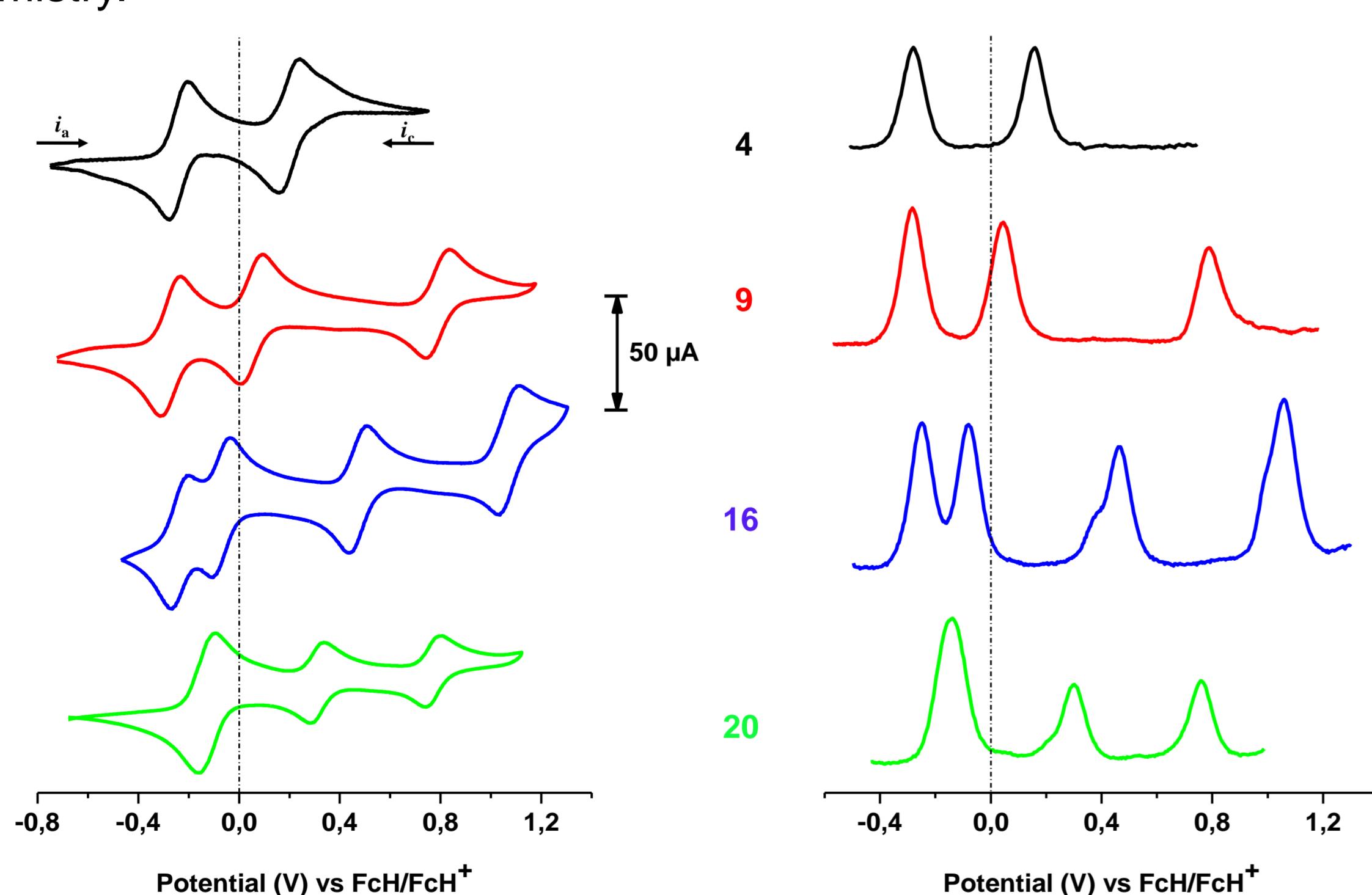
**Tab. 1** Cyclic Voltammetry Data (potentials vs  $\text{FcH}/\text{FcH}^+$ ), scan rate 100 mV·s<sup>-1</sup> at a glassy-carbon electrode of 1.0 mmol·L<sup>-1</sup> solutions of the analytes in dry dichloromethane containing 0.1 mol·L<sup>-1</sup> of  $[\text{N}^{\text{t}}\text{Bu}_4]\text{B}(\text{C}_6\text{F}_5)_4$  as supporting electrolyte at 25 °C.

Compd.	$E_1'$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$E_2'$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$E_3'$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$E_4'$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$\Delta E_1'$ (mV) <sup>[c]</sup>	$\Delta E_2'$ (mV) <sup>[c]</sup>	$\Delta E_3'$ (mV) <sup>[c]</sup>
4	-245 (66)	205 (82)	-	-	450	-	-
9	-280 (72)	5 (91)	790 (97)	-	285	785	-
16	-230 (64)	-70 (68)	470 (72)	1075 (79)	160	540	605
20	-130 (66)	310 (54)	770 (60)	-	440	460	-

<sup>a</sup>  $E'$  = oxidation process. <sup>b</sup>  $\Delta E_p$  = difference between oxidation and reduction potential. <sup>c</sup>  $\Delta E''$  = potential difference between two redox processes.

The redox properties of the ferrocenyl-substituted (oligo)pyrroles **4**, **9**, **16** and **20** have been determined by cyclic voltammetry and square-wave voltammetry (Fig. 2). The application of  $[\text{N}^{\text{t}}\text{Bu}_4]\text{B}(\text{C}_6\text{F}_5)_4$  as electrolyte allows the separate oxidation of all ferrocenyl termini except for diferrocenyl quarterpyrrol **20**. There the ferrocenyls were oxidized simultaneously, generating the dicationic species. In addition, 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 redox splitting decreases due to the increased chain length and therefore, the larger metal-metal distance. This behavior assumes a decreasing intermetallic communication, which was proven by spectroelectrochemistry.

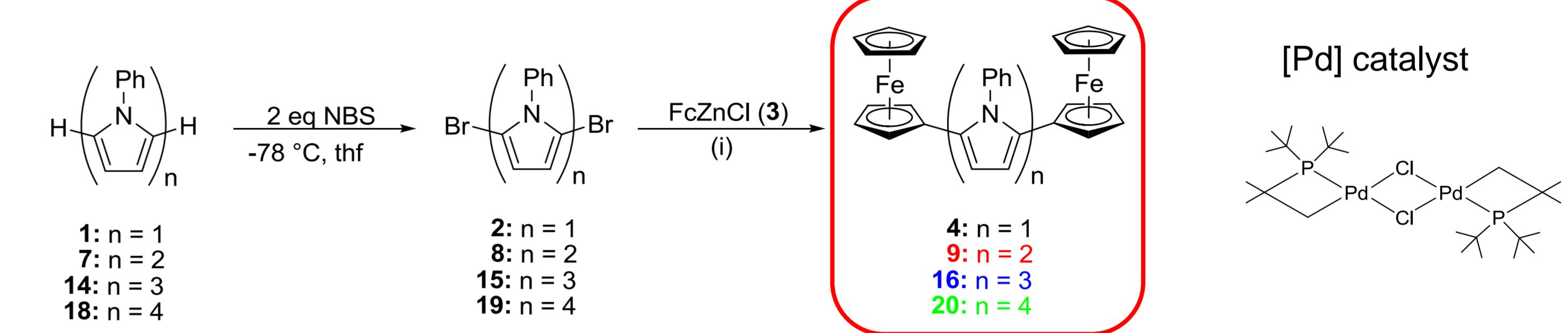


**Fig. 2** Cyclic voltammograms (scan rate: 100 mV·s<sup>-1</sup>) and square-wave voltammograms (scan rate: 2 mV·s<sup>-1</sup>) of dichloromethane solutions containing 1.0 mmol·L<sup>-1</sup> of **4**, **9**, **16** and **20** at 25 °C. Supporting electrolyte  $[\text{N}^{\text{t}}\text{Bu}_4]\text{B}(\text{C}_6\text{F}_5)_4$  (0.1 mol·L<sup>-1</sup>).

## Conclusion

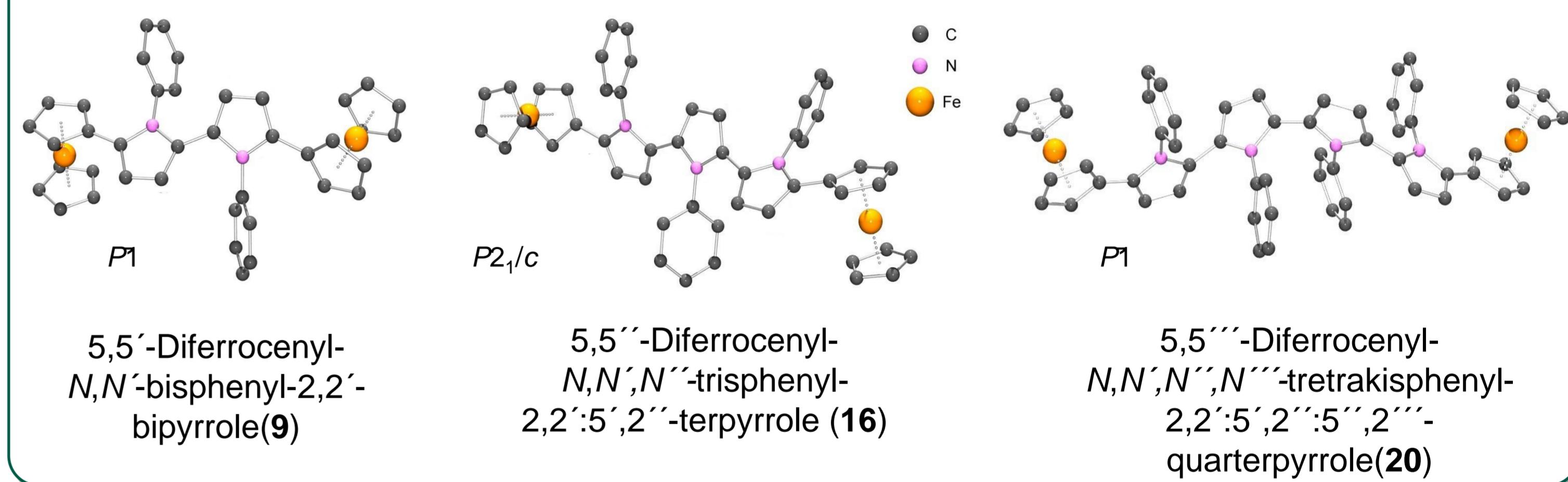
A series of diferrocenyl (oligo)pyrroles have been prepared using the Negishi ferrocenyl-ation reaction of halogenated heteroaromatics with ferrocenyl zinc chloride. The cyclic and square wave voltammograms highlight the electrochemical behavior of the organometallic compounds. Additionally, UV-Vis/NIR measurements revealed that the electronic interactions between the ferrocenyl termini in the mixed-valent species decrease with increasing chain length. The diferrocenyl (oligo)pyrroles **4**, **9** and **16** can be classified as moderately-coupled<sup>[1a]</sup> class II systems according to Robin and Day<sup>[7]</sup>, while the class I system **20** showed an absorption excited by inter ligand charge transfer.

## Synthesis and Characterization

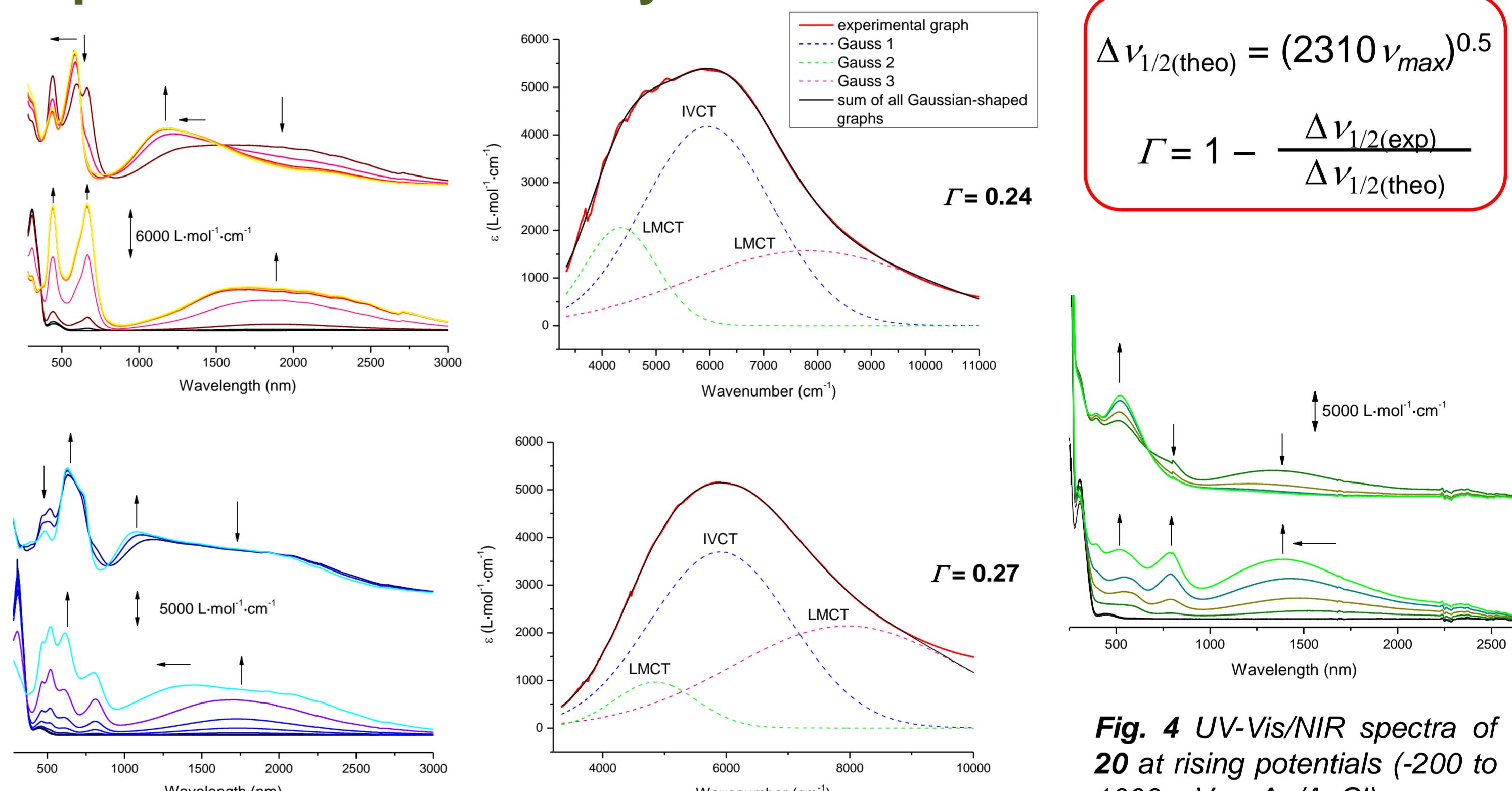


**Fig. 1** Synthesis procedure for diferrocenyl-substituted (oligo)pyrroles by Negishi C,C cross-coupling reactions; (i): 60 °C, 12 h, tetrahydrofuran, 0.25 mol% [Pd]-cat.

After appropriate work-up, the ferrocenyl-substituted compounds could be obtained as orange solids. They have been identified by NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{1}\text{H}$ ) and IR spectroscopy as well as elemental analysis. Additionally, high resolution ESI-TOF mass spectrometric and single crystal X-ray diffraction studies have been determined.



## Spectroelectrochemistry



**Fig. 4** UV-Vis/NIR spectra of **20** at rising potentials (-200 to 1000 mV vs Ag/AgCl).  $\Delta \nu_{1/2}(\text{theo}) = (2310 \nu_{\text{max}})^{0.5}$   
 $\Gamma = 1 - \frac{\Delta \nu_{1/2}(\text{exp})}{\Delta \nu_{1/2}(\text{theo})}$

**Fig. 3** UV-Vis/NIR spectra of **9** (top) and **16** (bottom) at rising potentials (-200 to 1000 mV vs Ag/AgCl) (left); deconvolution of the NIR spectrum of *in situ* generated **9<sup>+</sup>** (175 mV, top) and **16<sup>+</sup>** (250 mV, bottom) using three Gaussian-shaped bands (right). Measurement conditions: 25 °C, dichloromethane, 0.1 mol·L<sup>-1</sup>  $[\text{N}^{\text{t}}\text{Bu}_4]\text{B}(\text{C}_6\text{F}_5)_4$ . Arrows indicate increasing or decreasing absorptions.

The spectroelectrochemical investigations were carried out in an OTTLE cell (= Optical Transparent Thin-Layer Electrochemistry). Band shape analyses of the IVCT absorption were performed according to the Hush model for symmetric mixed-valent species<sup>[6]</sup> using the classification criterion of Brunschwig, Creutz and Sutin.<sup>[1a]</sup> For compound **20** an absorption was observed in NIR region but the bandmaximum ( $\nu_{\text{max}}$ ) shifts, indicating an inter ligand charge transfer. IVCT absorptions in the monocationic oxidation state: 4900 (**4**), 4180 (**9**), 3700 L·mol<sup>-1</sup>·cm<sup>-1</sup> (**16**).

## References and Acknowledgement

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