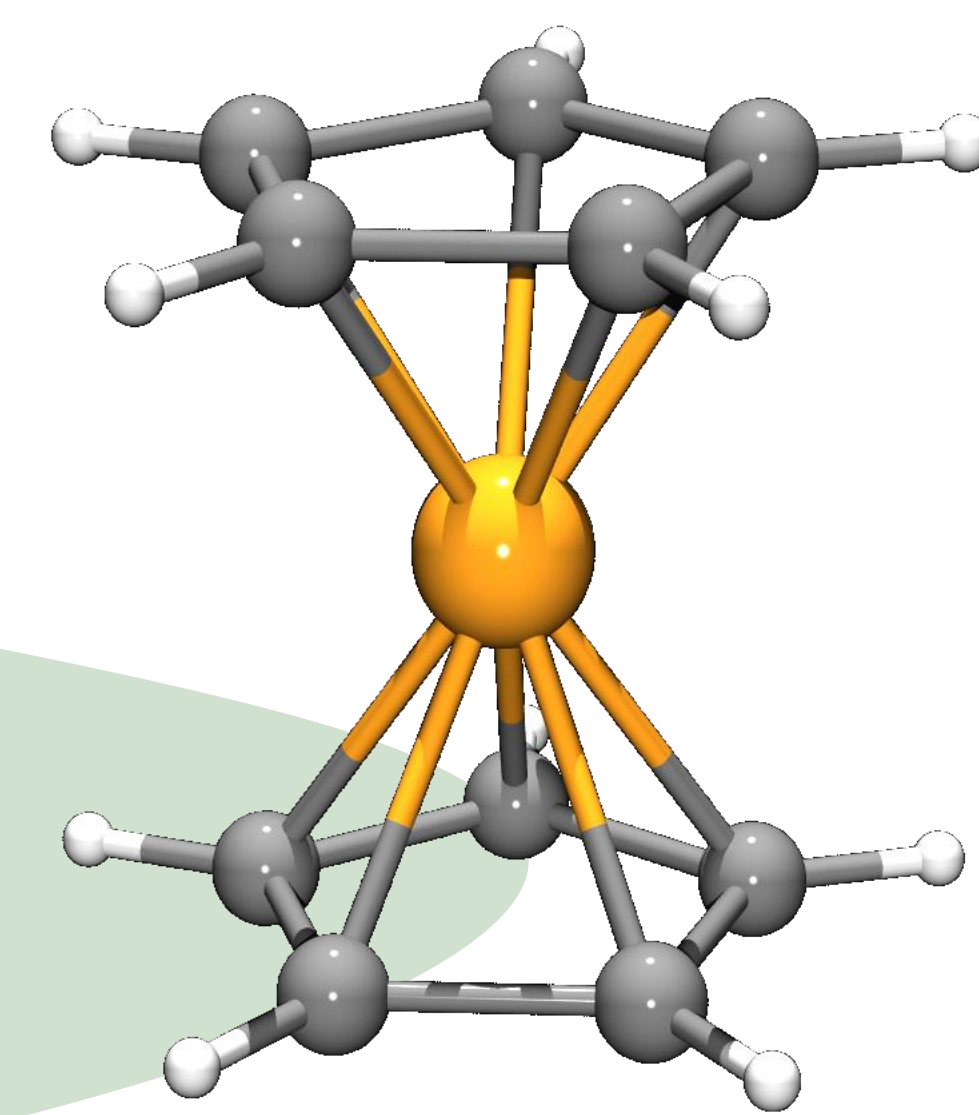


# Diferrocenyl (Oligo)pyrroles Influencing Electronic Intercommunication

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## Introduction

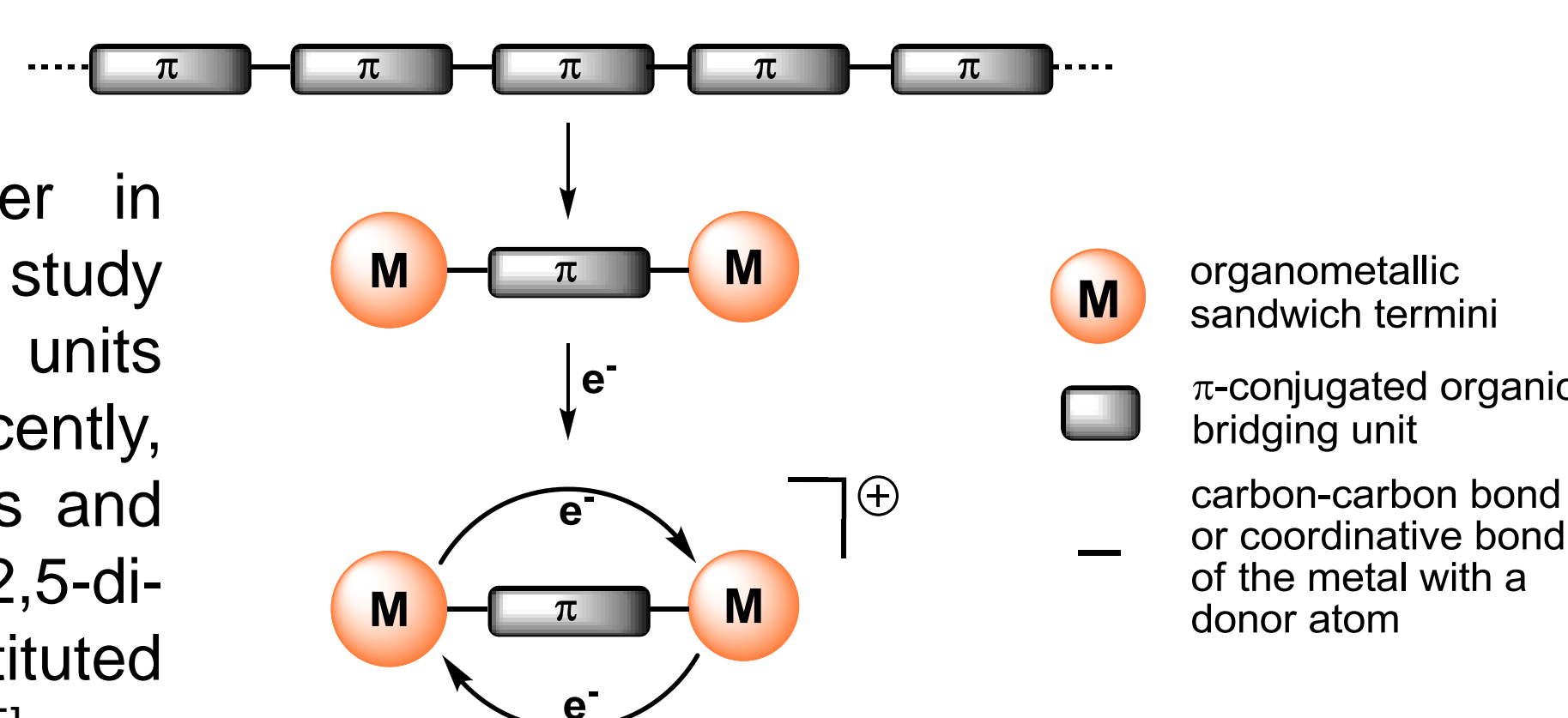
During recent years the development of compounds with redox-active metal centres has attracted considerable attention since they can be applied as new materials with novel chemical, physical and/or electronic properties in the field of material science.<sup>[1]</sup> Therefore, homo- and heterodinuclear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

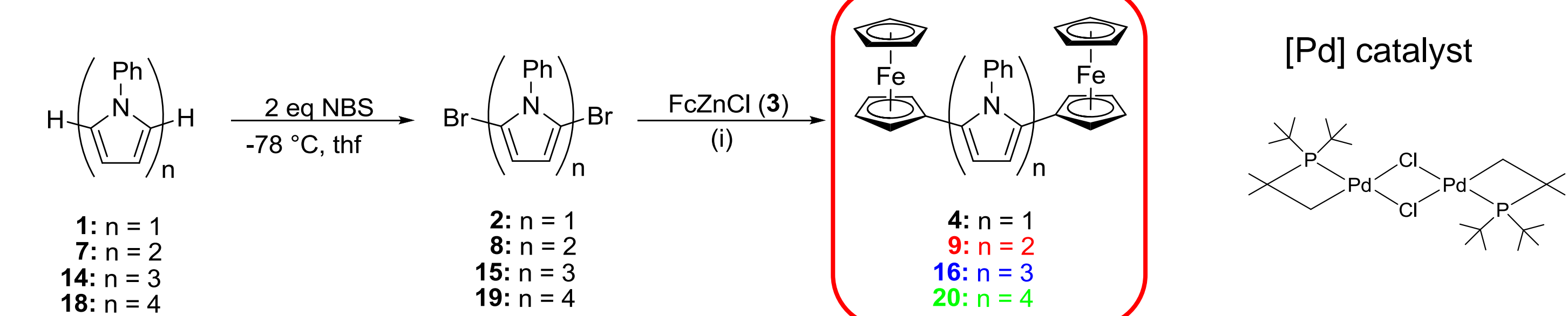
## Motivation

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.

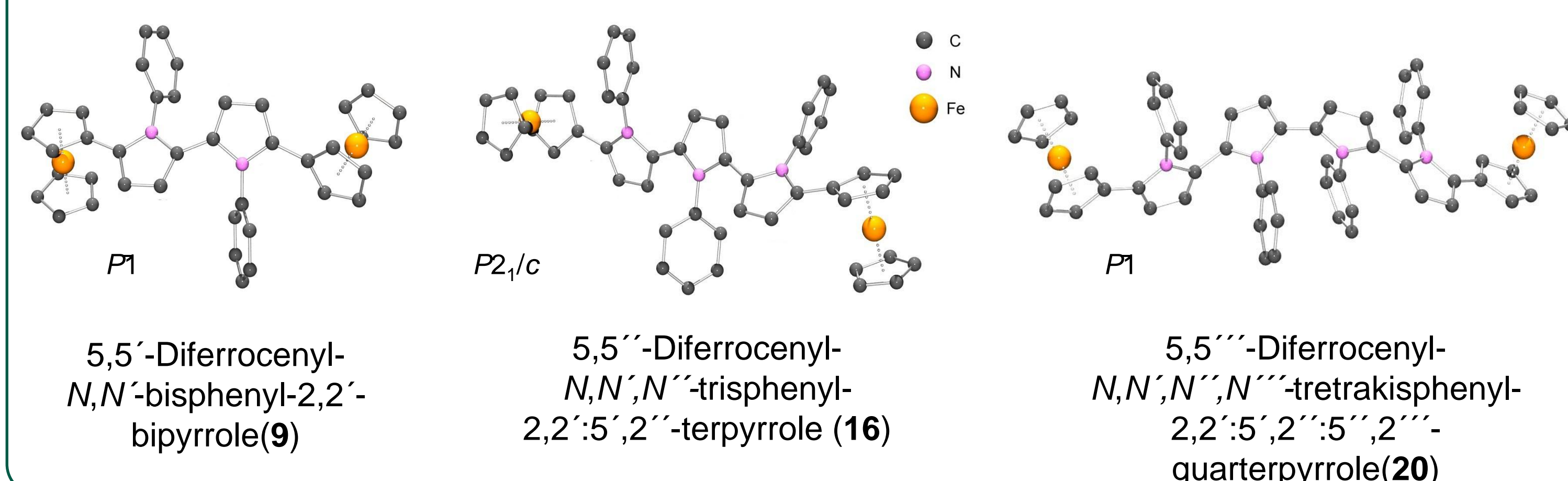


## Synthesis and Characterization



**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.



## Electrochemistry

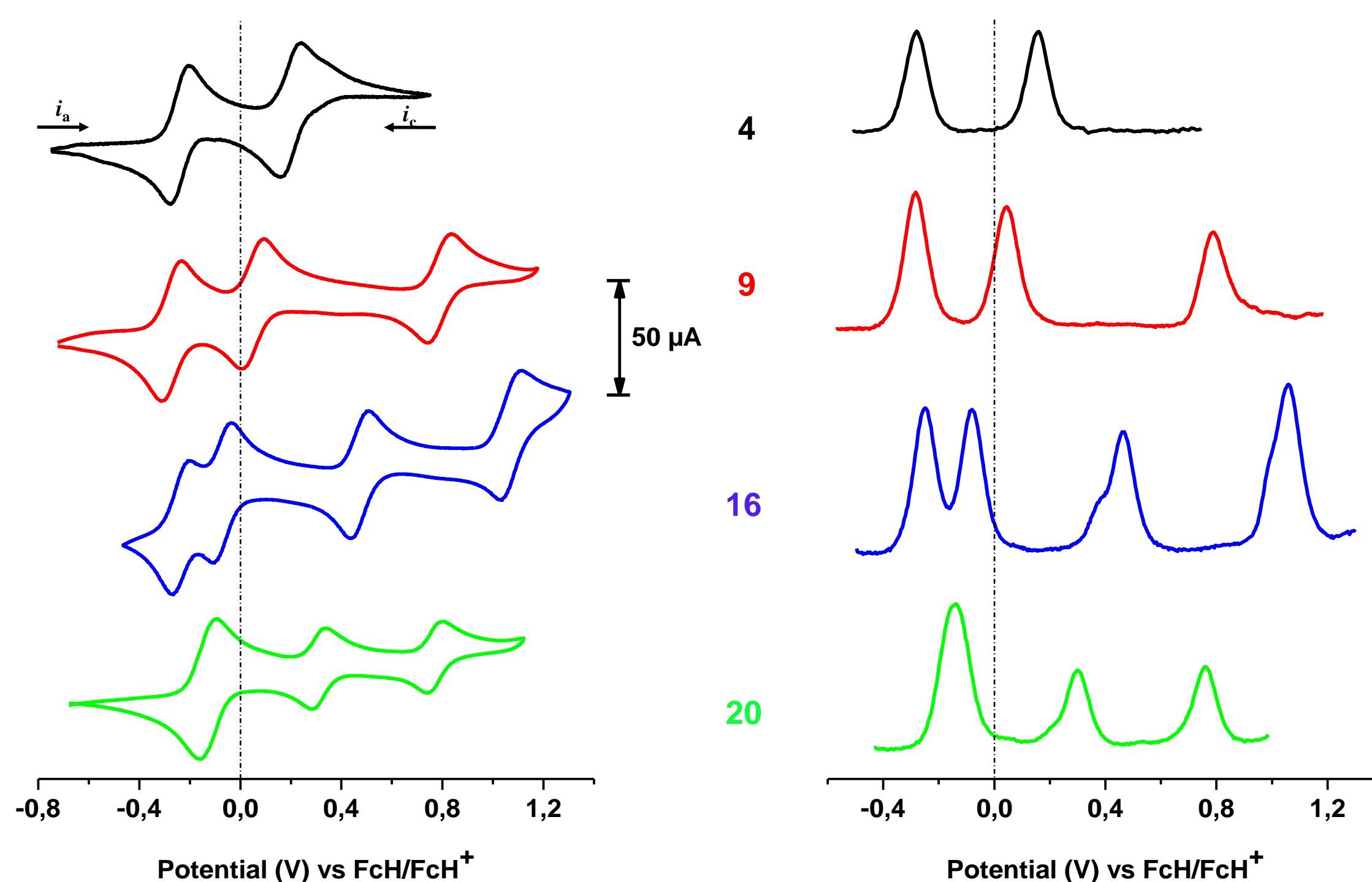
**Tab. 1** Cyclic Voltammetry Data (potentials vs FcH/FcH<sup>+</sup>, scan rate 100 mV·s<sup>-1</sup> at a glassy-carbon electrode of 1.0 mmol·L<sup>-1</sup> solutions of the analytes in dry dichloromethane containing 0.1 mol·L<sup>-1</sup> of [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte at 25 °C.

Compd.	$E_1^{\circ'}$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$E_2^{\circ'}$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$E_3^{\circ'}$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$E_4^{\circ'}$ (mV) <sup>[a]</sup> ( $\Delta E_p$ (mV)) <sup>[b]</sup>	$\Delta E_1^{\circ'}$ (mV) <sup>[c]</sup>	$\Delta E_2^{\circ'}$ (mV) <sup>[c]</sup>	$\Delta E_3^{\circ'}$ (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>  $E^{\circ'}$  = oxidation process. <sup>b</sup>  $\Delta E_p$  = difference between oxidation and reduction potential. <sup>c</sup>  $\Delta E^{\circ'}$  = potential difference between two redox processes.

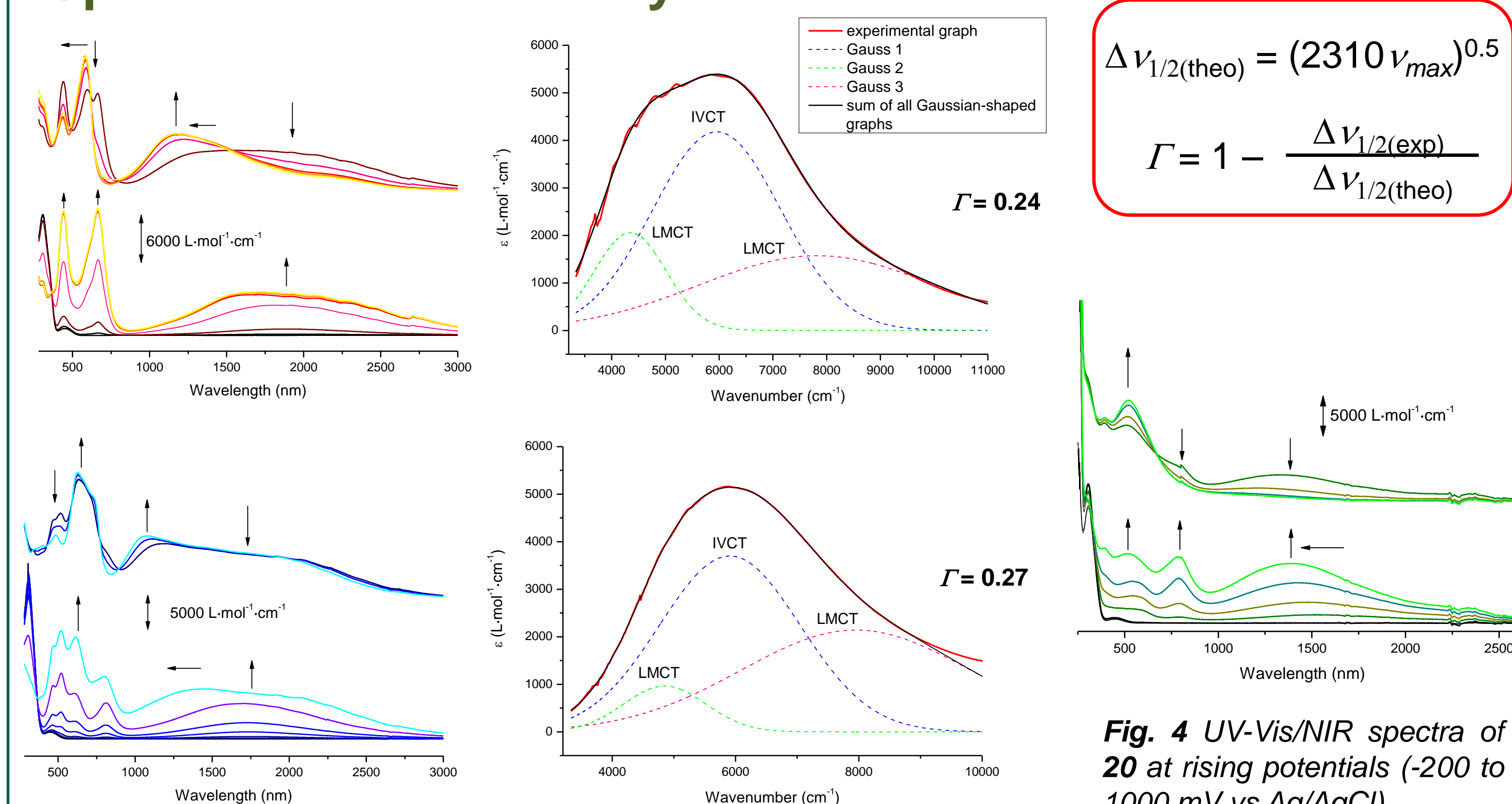
The redox properties of the ferrocenyl-substituted (oligo)pyrroles **4**, **9**, **16** and **20** have been determined by cyclic voltammetry and square-wave voltammetry (Fig. 2). The application of [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as electrolyte allows the separate oxidation of all ferrocenyl termini except for diferrocenyl quaterpyrrol **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 [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.1 mol·L<sup>-1</sup>).

## Spectroelectrochemistry



**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\*** (175 mV, top) and **16\*** (250 mV, bottom) using three Gaussian-shaped bands (right). Measurement conditions: 25 °C, dichloromethane, 0.1 mol·L<sup>-1</sup> [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Arrows indicate increasing or decreasing absorbances.

The spectroelectrochemical investigations were carried out in an OTTE 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 Brunswig, 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**).

## 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.

## References and Acknowledgement

- [1] (a) Brunswig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168–184; (b) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. *Coord. Chem. Rev.* **2004**, *248*, 683–724.
- [2] (a) Sato, M.; Fukui, K. *Synth. Met.* **2007**, *157*, 619–626; (b) Sato, M.; Kamine, H. *Chem. Lett.* **2009**, *38*, 924–925.
- [3] (a) Molina *et al.* *Inorg. Chem.*, **2007**, *46*, 825–838; (b) Robertson, N.; McGowan, G. A. *Chem. Soc. Rev.* **2003**, *32*, 96–103.
- [4] Hildebrandt, A.; Pfaff, U.; Lang, H. *Rev. Inorg. Chem.* **2011**, *31*, 111–141.
- [5] Hildebrandt, A.; Schaarschmidt, D.; Claus, R.; Lang, H. *Inorg. Chem.* **2011**, *50*, 10623–10632.
- [6] Hush, N. S. *Electrochim. Acta*, **1968**, *13*, 1005–1023.
- [7] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.*, **1967**, *10*, 247–422.

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