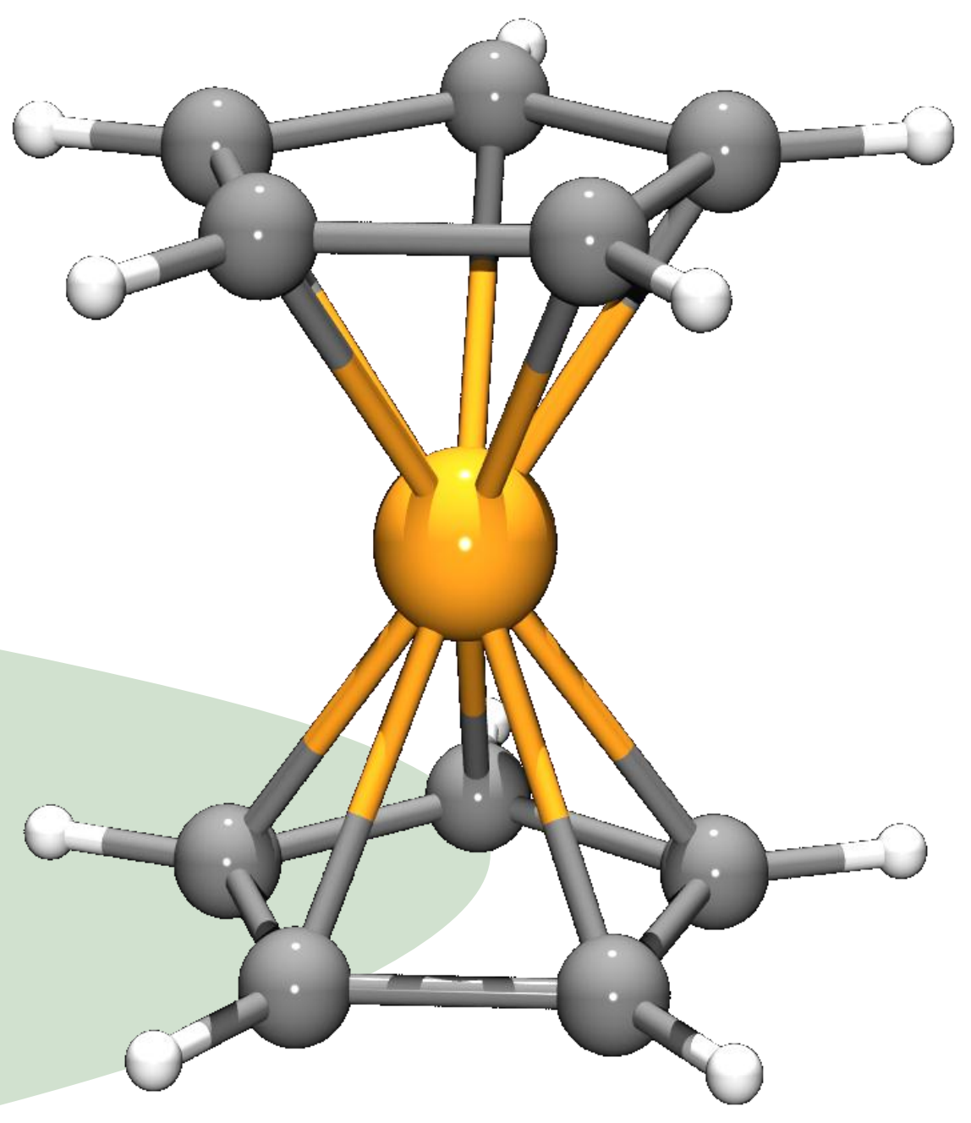

Modifying the Electronic Communication in 2,5-Diferrocenyl Five-Membered Heterocycles

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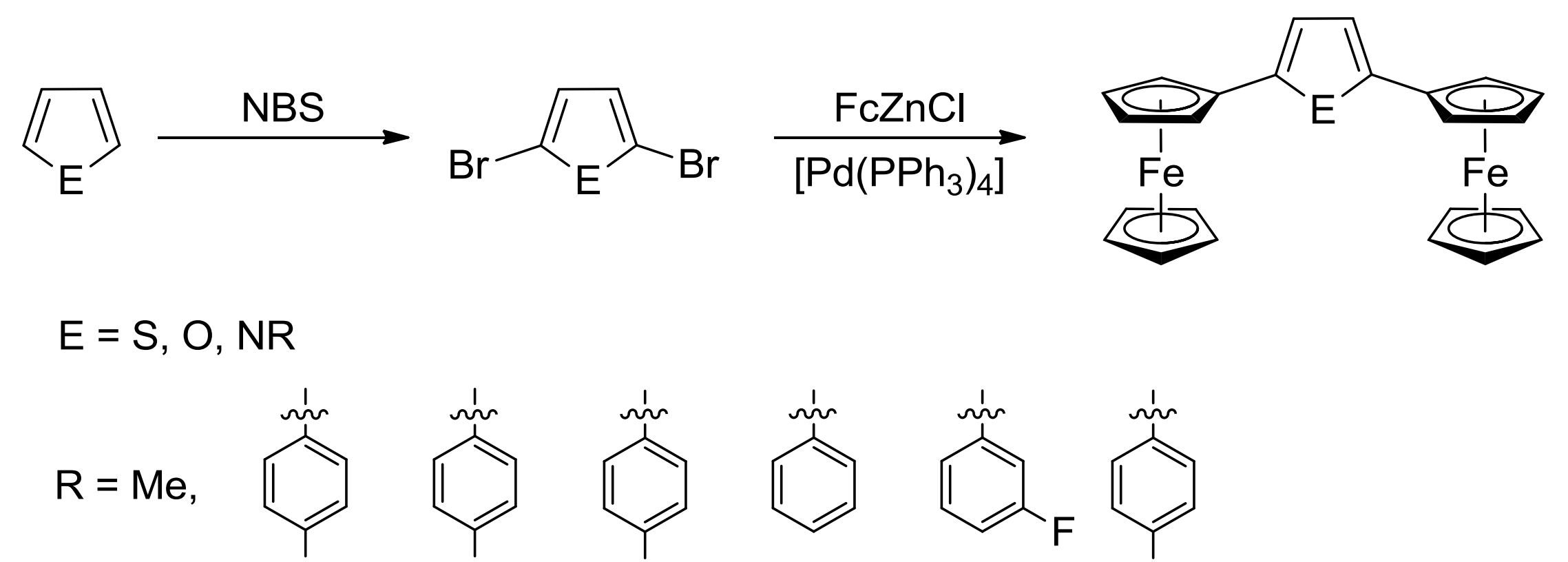
Introduction

During recent years mixed-valent species have drawn increasing interest because they can be used as model systems to study electron transfer through π-conjugated carbon-rich organic linking units and hence may be used for the design of novel electro-active materials. [1]

For our contribution in this field of research, we dedicated our efforts to the spectro-electrochemical properties of 2,5-diferrocenyl heterocycles. This family of compounds provided us with the possibility to change the electronic properties of the heterocyclic connector unit without changing the geometrical set up between the redox active ferrocenyl units and therefore, without changing their electrostatic interactions. This should enable to draw comparative conclusions regarding the communication properties simply by recording cyclic voltammogramms.

Synthesis and Characterization



Scheme 1. Synthesis of 2,5-diferrocenyl heterocycles (NBS = *N*-bromosuccinimde, Fc = Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)).

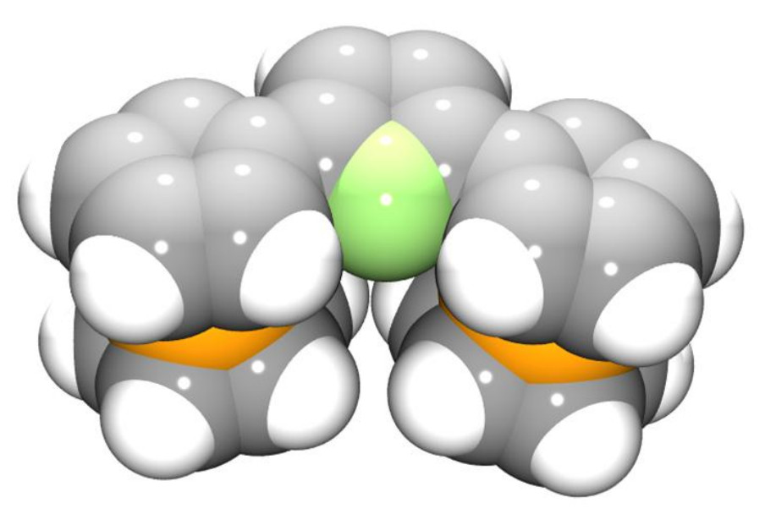


Figure 1. Molecular structure of 2,5-diferrocenyl furan.

The 2,5-diferrocenyl heterocycles have been prepared by a two-fold Negishi cross-coupling reaction of the corresponding dibromo species, which were accessible by direct bromination of the heterocycles with *N*-bromosuccinimide and ferrocenyl zinc chloride prepared by reaction of monolithioferrocene and anhydrous zinc chloride. The compounds could be isolated in good yields (60 – 80 %) and are characterized among others by NMR, IR and mass spectrometry.

Electrochemistry

The electrochemistry experiments (CV, SWV) have been conducted in dry dichloromethane solutions of the respective analyte (0.5 mmol·L^{-1}) and [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol·L^{-1}) at scan rates of 100 mV·s^{-1} (CV). All potentials were referenced to the FcH/FcH$^+$ redox couple ($E°'$ = 0 mV) and are summarized in Table 1. As representative example the cyclic voltammogram of 2,5-diferrocenyl-*N*-methyl pyrrole is shown in Figure 2. The ferrocenyl units in each compound of this series are oxidized step-wisely, indicating interactions between the redox active termini. The redox splitting between those two redox events in the molecules seems to be highly dependent on the electronic properties of the heterocyclic ring. To clarify the nature of these interactions spectro-electochemical studies have additionally been carried out.

Table 1. Electrochemical data of the 2,5-diferrocenyl heterocycles.

Comp.			$E_1°'$ (mV) (ΔE_p (mV))	$E_2°'$ (mV) (ΔE_p (mV))	$\Delta E°'$ (mV)
E =		S	- 94 (65)	166 (65)	260
		O	-152 (60)	138 (63)	290
E = NR	R =	Me	-206 (65)	204 (65)	410
		C$_6$H$_4$-*p*-NMe$_2$	-305 (61)	175 (68)	480
		C$_6$H$_4$-*p*-OMe	-255 (60)	205 (69)	460
		C$_6$H$_4$-*p*-Me	-250 (71)	205 (75)	455
		C$_6$H$_5$	-240 (68)	210 (75)	450
		C$_6$H$_4$-*m*-F	-210 (61)	215 (65)	425
		C$_6$H$_4$-*p*-CO$_2$Et	-190 (62)	230 (69)	420

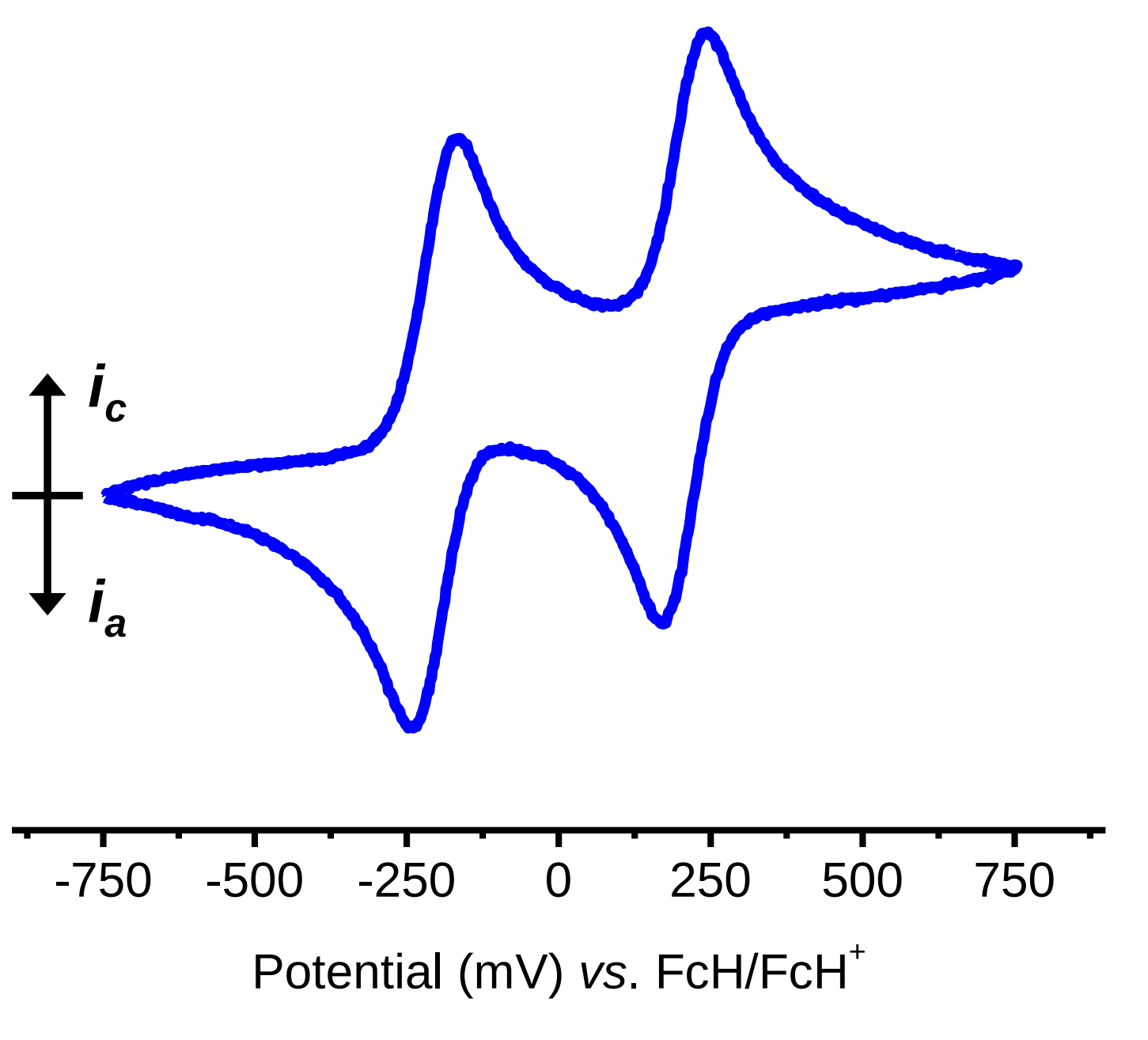


Figure 2. Cyclic voltammogram of 2,5-diferrocenyl-*N*-methyl pyrrole.

Theoretical Considerations

The redox splitting $\Delta E°'$ which could be observed in the electrochemical measurement is in direct relation to the Gibbs free energy of comproportionation $\Delta G_c°$ of the mixed-valent compound. Four factors contribute to the magnitude of $\Delta G_c°$: (i) a statistical contribution, (ii) an electrostatic factor (ΔG_e), (iii) a synergistic factor (ΔG_s), and (iv) the Gibbs free energy of resonance stabilization (ΔG_r) (eq. 1). Taking into account that the geometry of the here shown series of molecules is almost identical, eq.1 could be simplified to give eq. 2.

$$\Delta G_c^o = -\Delta E^{o'} \cdot F = \underbrace{\tfrac{1}{2}RT \ln \tfrac{1}{4} + \Delta G_e + \Delta G_s}_{} + \Delta G_r \qquad (1)$$

$$\Delta G_c^o = -\Delta E^{o'} \cdot F = \qquad const \qquad + \Delta G_r \qquad (2)$$

In eq. 3 it is shown that ΔG_r is, within the class II regime, also related to the electronic coupling parameter H_{ab}. This relation connects the electrochemical properties with the spectroscopic ones. Combining equations 2, 3 and 4 leads to a linear relationship between the redox splitting and the oscillator strength *f* of the IVCT absorption in eq. 5.

$$-\Delta G_r = \frac{2H_{ab}^2}{v_{max}} \qquad (3) \qquad\qquad H_{ab} = 2.06 \cdot 10^{-2} \frac{\sqrt{v_{max} \cdot \varepsilon_{max} \cdot \Delta v_{1/2}}}{r_{ab}} \qquad (4)$$

$$\boldsymbol{f = \frac{\varepsilon_{max} \cdot \Delta v_{1/2}}{4.6 \cdot 10^9} = \frac{const \cdot r_{ab}^2 \cdot 4.6 \cdot 10^{-9}}{8.49 \cdot 10^{-4}} + \frac{F \cdot r_{ab}^2 \cdot 4.6 \cdot 10^{-9}}{8.49 \cdot 10^{-4}} \cdot \Delta E°'} \qquad (5)$$

It is possible to estimate the effective electron transfer distance r_{ab} from the slope of this linear relationship using eq. 6. This value is notoriously difficult to obtain experimentally.

$$r_{ab} = \sqrt{m \frac{8.49 \cdot 10^{-4}}{F \cdot 4.6 \cdot 10^{-9}}} \qquad (6)$$

Spectro-electrochemistry

The spectro-electrochemical studies were performed by stepwise increase of the potential from -500 to 1200 mV *vs* Ag/AgCl in an OTTLE cell (OTTLE = Optically Transparent Thin-Layer Electrochemical) containing dichloromethane solutions of the respective analytes (1.0 mmol·L^{-1}) and [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol·L^{-1}) as electrolyte. During this process each of the molecules showed intense absorptions in the NIR-region of the spectrum in its mono-cationic oxidation state (Figure 3). To determine the physical parameters (ε_{max}, $\Delta v_{1/2}$ and v_{max}) of this IVCT band a deconvolution using two Gaussian shaped absorptions and a background correction was performed (Figure 4). The extinctions of the IVCT bands of the molecules of this series showed a similar trend as observed for the redox splitting determined by cyclic voltammetry.

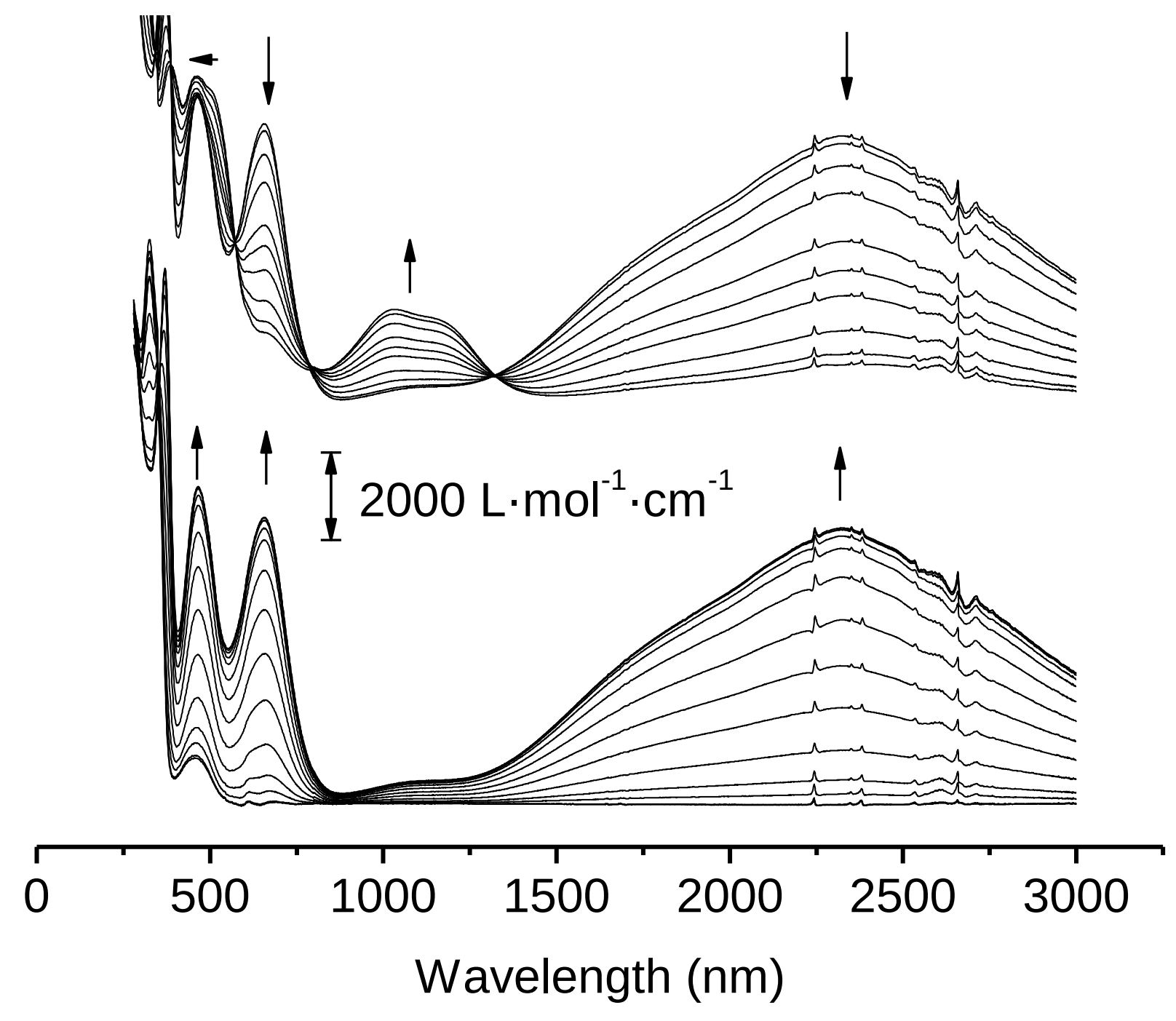


Figure 3. NIR spectra of 2,5-diferrocenyl-*N*-tolyl pyrrole at rising potentials (bottom: -200 to 300 mV; top: 250 to 900 mV *vs* Ag/AgCl).

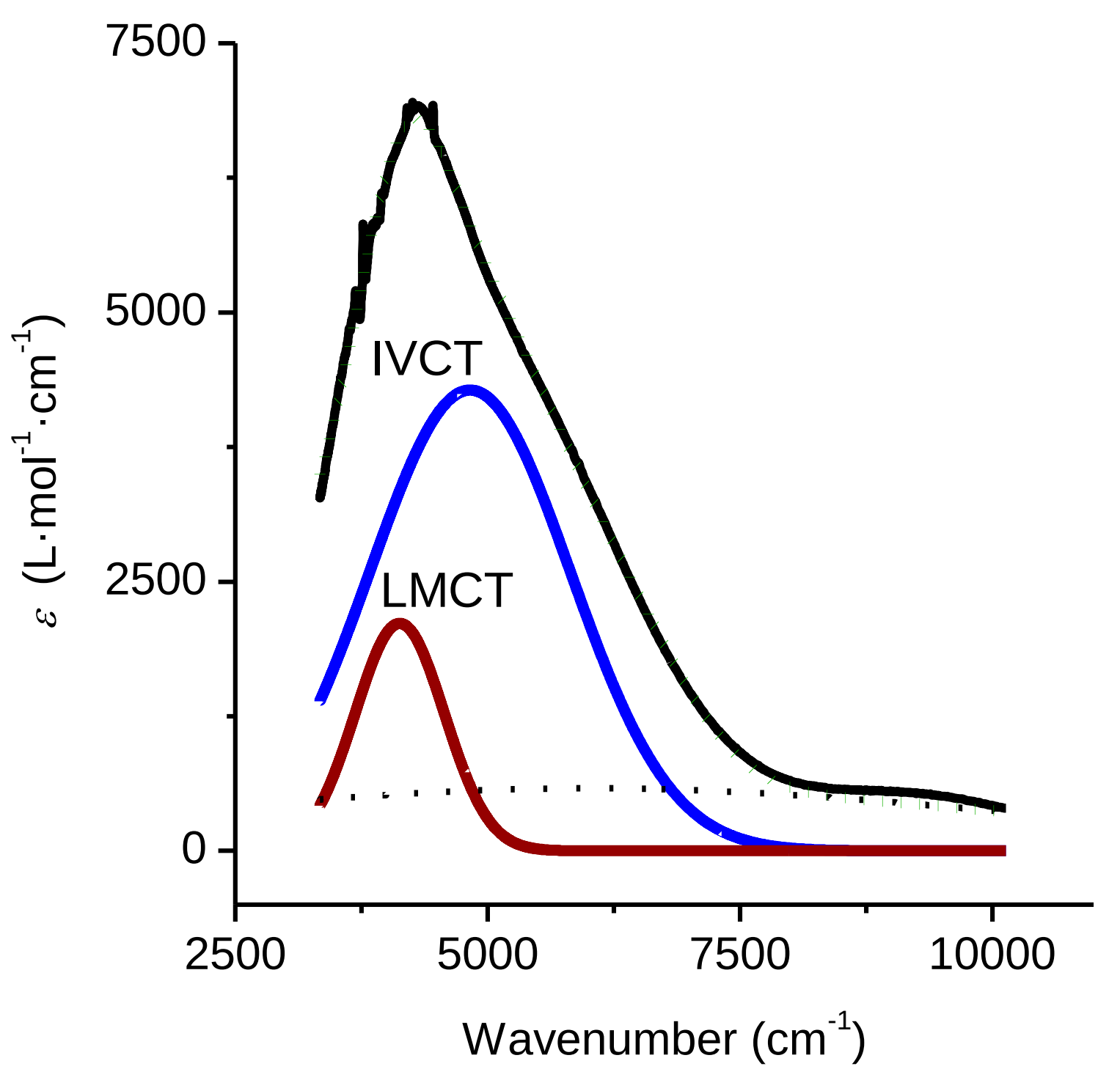


Figure 4. Deconvolution of the NIR spectrum of 2,5-diferrocenyl-*N*-tolyl pyrrole in its mono-cationic oxidation state.

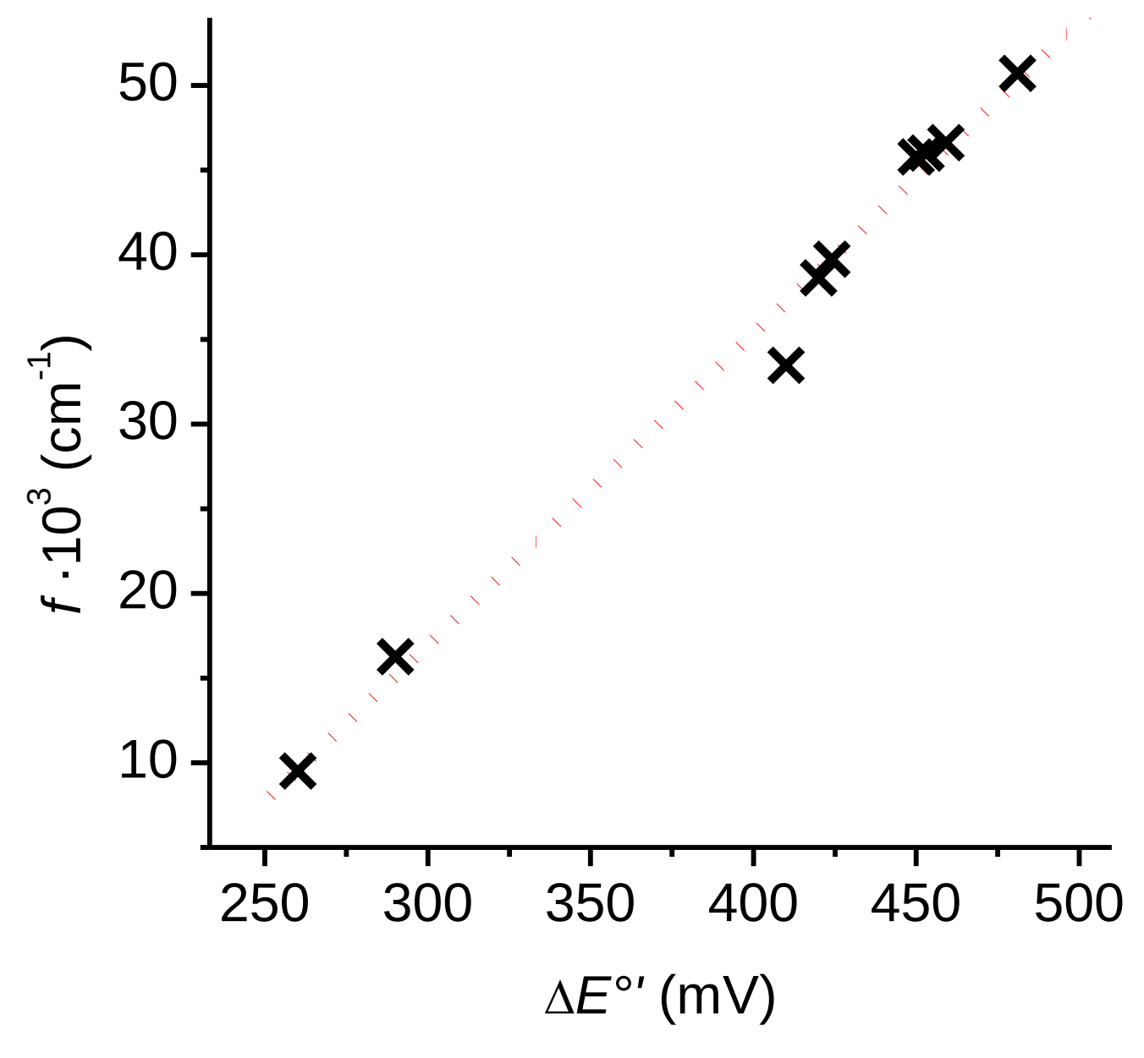


Figure 5. Correlation of the oscillator strength *f* of the IVCT band and the redox splitting $\Delta E°'$.

Plotting the oscillator strength *f* of the IVCT band versus the redox splitting $\Delta E°'$ leads in agreement with our theoretical considerations to a linear relationship (Figure 5). Using eq. 6 the effective electron transfer distance r_{ab} for this series of heterocycles could be calculated to

r_{ab} = 2.0 ± 0.1 Å

This value is much less than the geometrical iron-iron distance which could be determined for 2,5-diferrocenyl furan to 6.3 Å. Due to partly delocalization of the "redox orbital" into the heterocycle, r_{ab} is expected to be much shorter.

Conclusion

A series of 2,5-diferrocenyl heterocycles have been synthesized *via* Negishi cross-coupling reactions and their electrochemical behavior was studied extensively. The ferrocenyl termini of all molecules within this family of compounds are oxidized consecutively. NIR studies revealed IVCT-processes in the mixed-valent oxidation state classifying these compounds as class II molecules according to Robin and Day. [3]

The uniform geometrical set-up, which caused similar electrostatic repulsions between the redox centers, allowed a linear relationship between the redox splitting $\Delta E°'$ (ranging from 260 to 480 mV) and the oscillator strength *f* of the IVCT absorption band. The slope of this linear relationship was used to develop a **new** approach for the calculation of the effective electron transfer distance r_{ab}, which was determined to be 2.0 ± 0.1 Å.

References and Acknowledgement

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