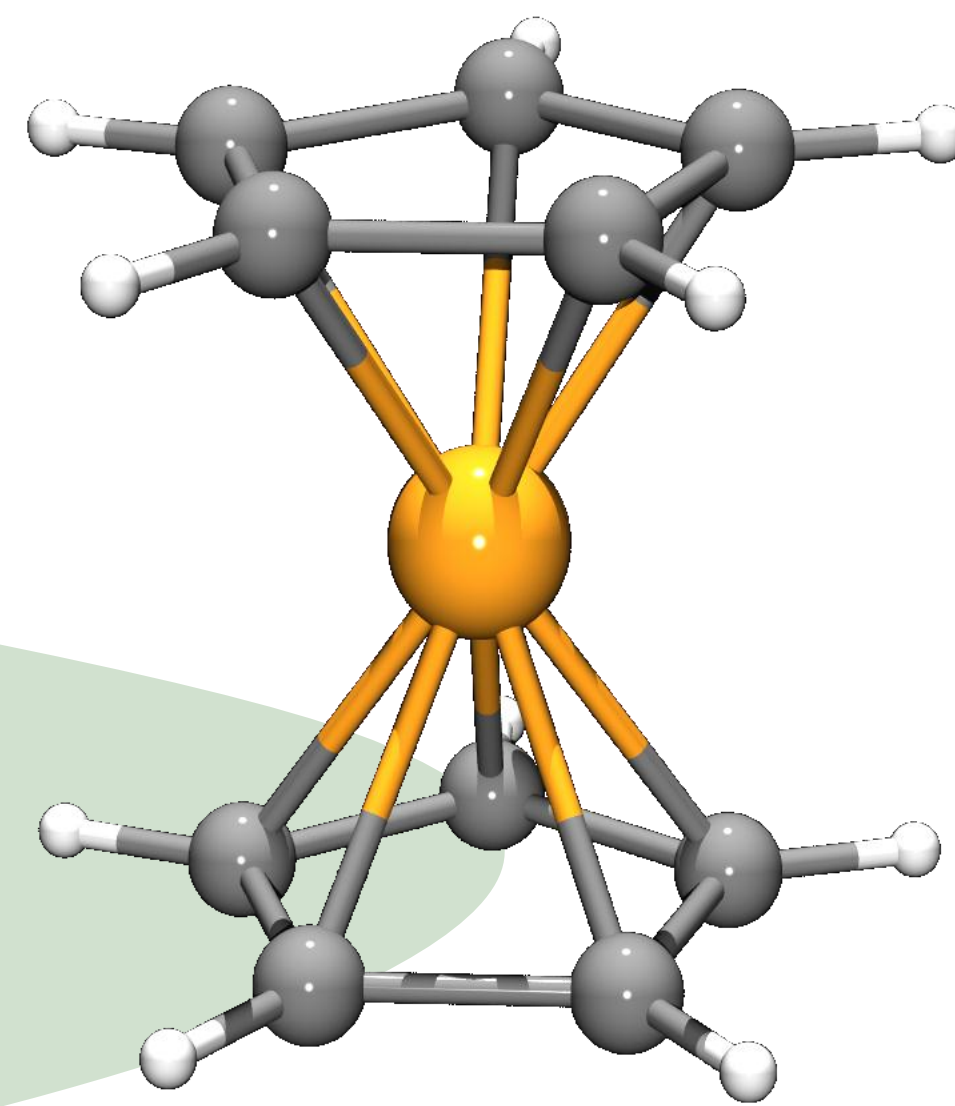




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# Influencing the electronic interaction in diferrocenyl functionalized pyrrole and thiophene derivatives



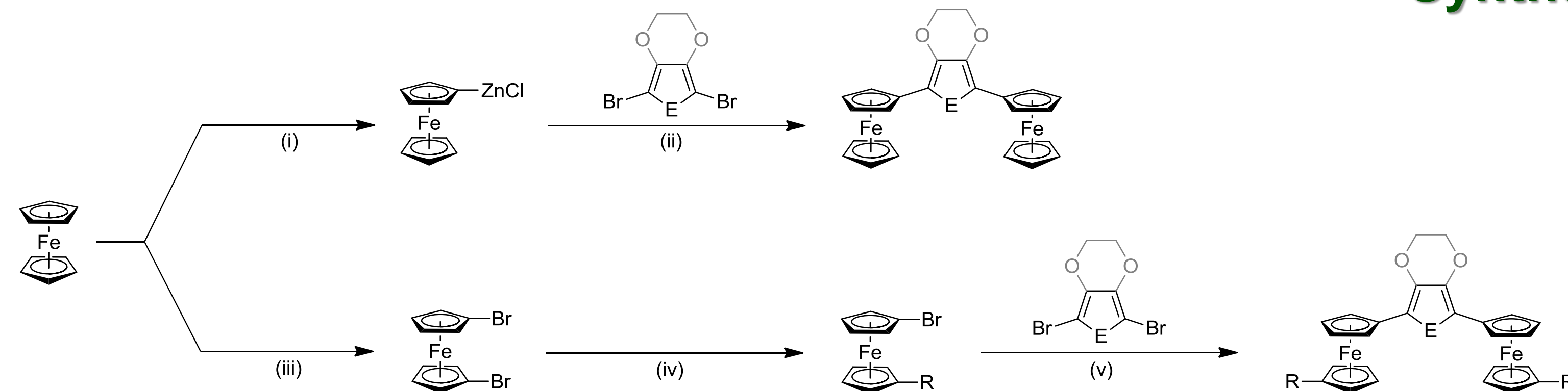
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## Introduction and Motivation

Molecules featuring at least two redox-active metal centres linked by homo- or hetero-aromatics can be used to generate mixed-valent species. Such systems can be promising candidates to design innovative electro-active materials such as semiconducting polymers or molecular wires. [1] Due to the good stability of ferrocene in its neutral- and oxidized-state, ferrocenyl-substituted hetero-aromatics have shown to be excellent models for electron transfer studies. [2] It could be demonstrated that the electronic structure of the heterocycle strongly influences the intermetallic communication within those systems. The electronic characteristics can be modified by substituents on the bridging unit as demonstrated previously. [3] In continuation of our work, we present herein the design and the electrochemical behavior of ferrocenyl substituted pyrroles and thiophenes, which are modified on the ferrocenyl termini as well as on the heterocycle itself. The influence of the substituents on charge transfer interactions is discussed.

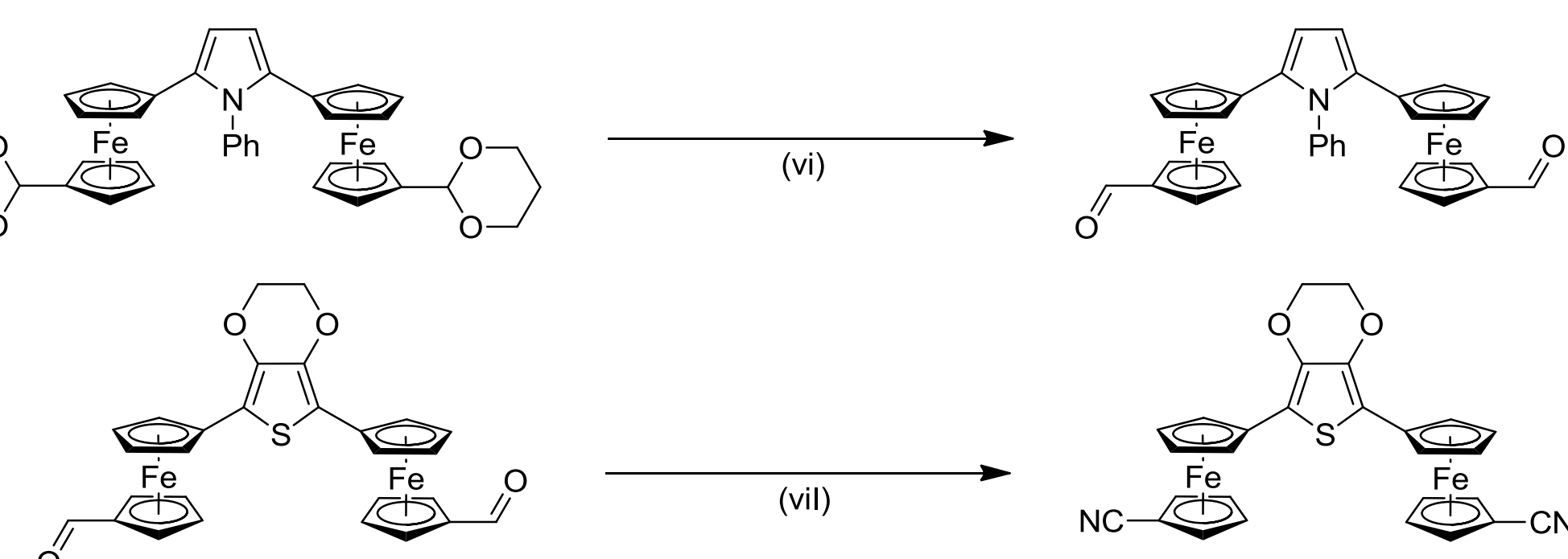
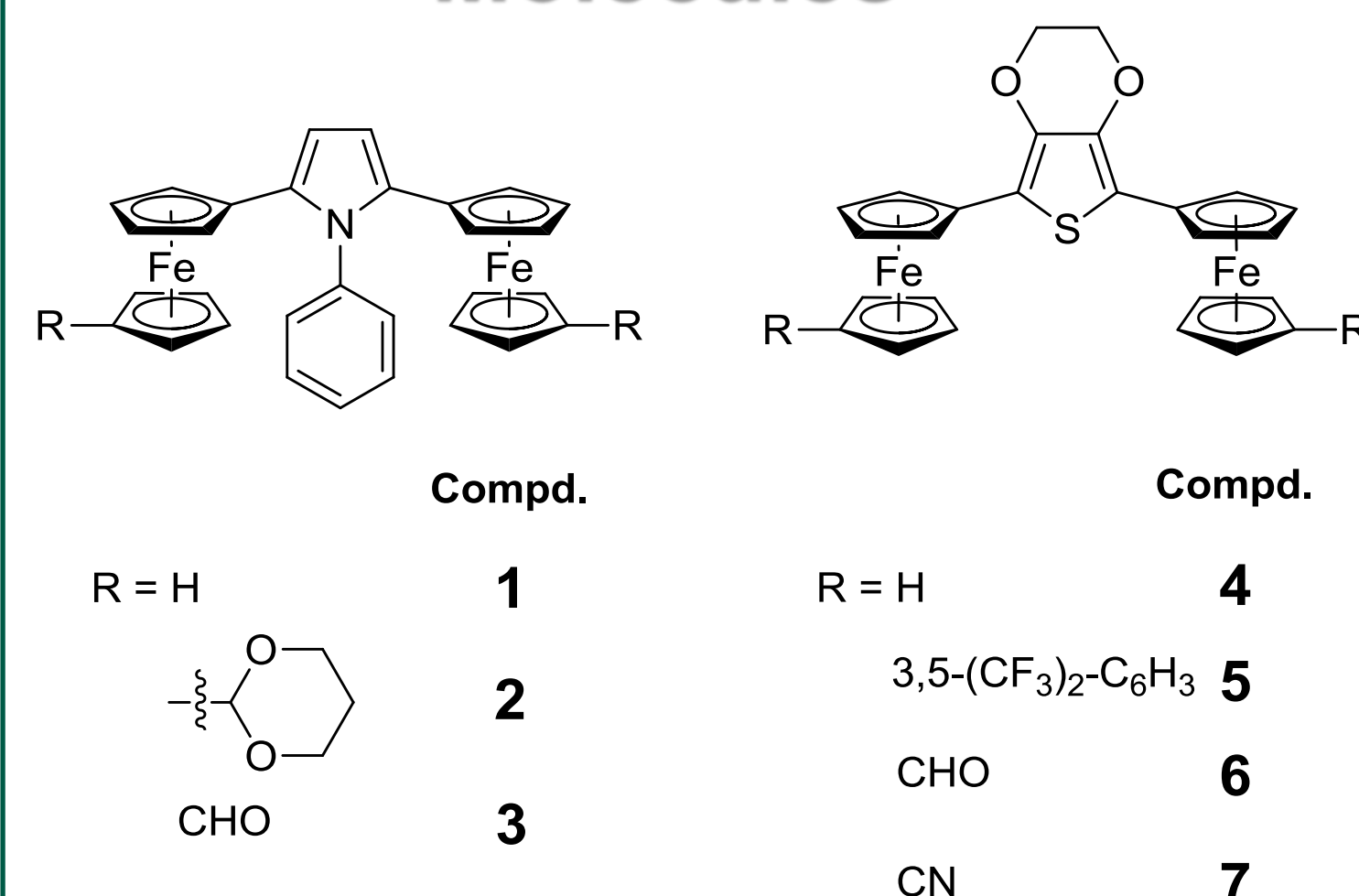
## Synthesis



**Scheme 1:** Synthesis of molecules **1**, **2**, **4**, **5** and **6**. Conditions: (i) thf; 1<sup>st</sup>: <sup>n</sup>BuLi, -80 °C, 1 h; 2<sup>nd</sup>: [ZnCl<sub>2</sub>·2thf], 0 °C, 30 min. (ii) 1<sup>st</sup>: 2,5-Dibromoheterocycle; 2<sup>nd</sup>: [Pd], 55 °C, 48 h ([Pd] = [Pd(CH<sub>2</sub>CHMe<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)(μ-Cl)]<sub>2</sub>). (iii) 1<sup>st</sup>: <sup>n</sup>BuLi/TMEDA, *n*-hexane, 25 °C, 20 h; 2<sup>nd</sup>: 1,1,2,2-tetrabromoethane, -80 °C, 3 h. (iv) thf; 1<sup>st</sup>: <sup>n</sup>BuLi, -80 °C, 45 min; 2<sup>nd</sup>: [ZnCl<sub>2</sub>·2thf], 0 °C, 30 min; 3<sup>rd</sup>: 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>Br; 4<sup>th</sup>: [Pd], 30 °C, 24 h (**5**). thf; 1<sup>st</sup>: <sup>n</sup>BuLi, -80 °C, 45 min; 2<sup>nd</sup>: DMF, 25 °C, 4 h; 3<sup>rd</sup>: toluene; 1,3-propanediol, *p*-toluenesulfonic acid, reflux, 24 h (**2**). thf; 1<sup>st</sup>: <sup>n</sup>BuLi, -80 °C, 45 min; 2<sup>nd</sup>: DMF, 25 °C, 4 h; 3<sup>rd</sup>: toluene; HC(OMe)<sub>3</sub>, *p*-toluenesulfonic acid, 25 °C, 12 h (**6**). (v) thf; 1<sup>st</sup>: <sup>n</sup>BuLi, -80 °C, 1 h; 2<sup>nd</sup>: [ZnCl<sub>2</sub>·2thf], 0 °C, 1 h; 3<sup>rd</sup>: 2,5-dibromoheterocycle, [Pd], 60 °C, 48 h.

➡ The diferrocenyl heterocycles **1** – **7** were synthesized applying a palladium-promoted Negishi C,C cross-coupling protocol, in which an organozinc compound was treated with the corresponding 2,5-dibromoheterocycle, as catalyst [Pd(CH<sub>2</sub>CHMe<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)(μ-Cl)]<sub>2</sub> was used. After appropriate work-up, including hydrolysis of acetals as well as the oximation-condensation reaction for nitrile synthesis, molecules **1** – **7** could be isolated as either orange or red solid materials (Scheme 1 and 2).

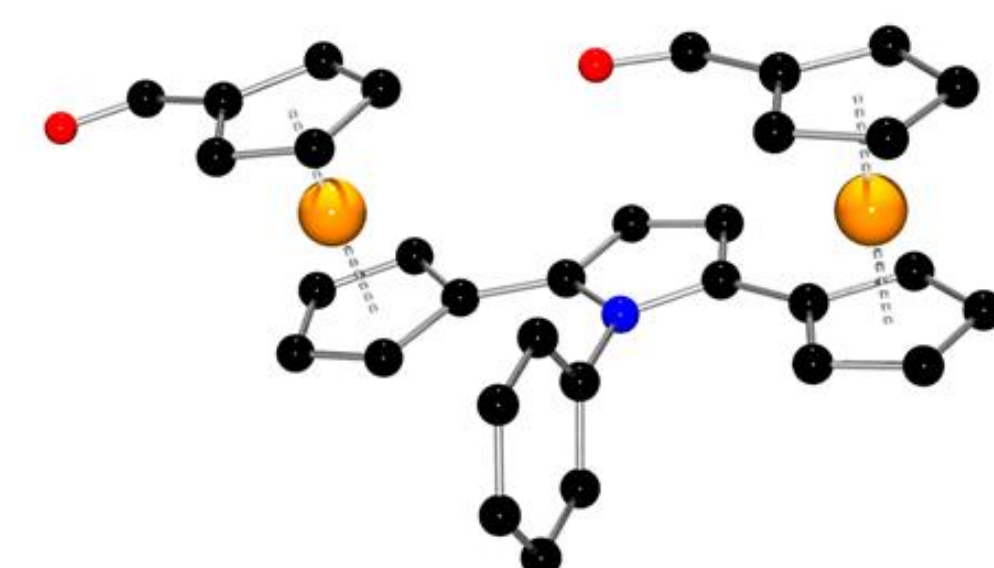
## Molecules [2]



**Scheme 2:** Synthesis of compounds **3** and **7**. Conditions: (vi) dichloromethane; *p*-toluenesulfonic acid, toluene, H<sub>2</sub>O, 40 °C, 24 h. (vii) Pyridine; 1<sup>st</sup>: NH<sub>2</sub>OH·HCl, H<sub>2</sub>O, CuSO<sub>4</sub>; 2<sup>nd</sup>: NEt<sub>3</sub>, *N,N*-dicyclohexylcarbodiimide (DCC), 25 °C, 12 h.

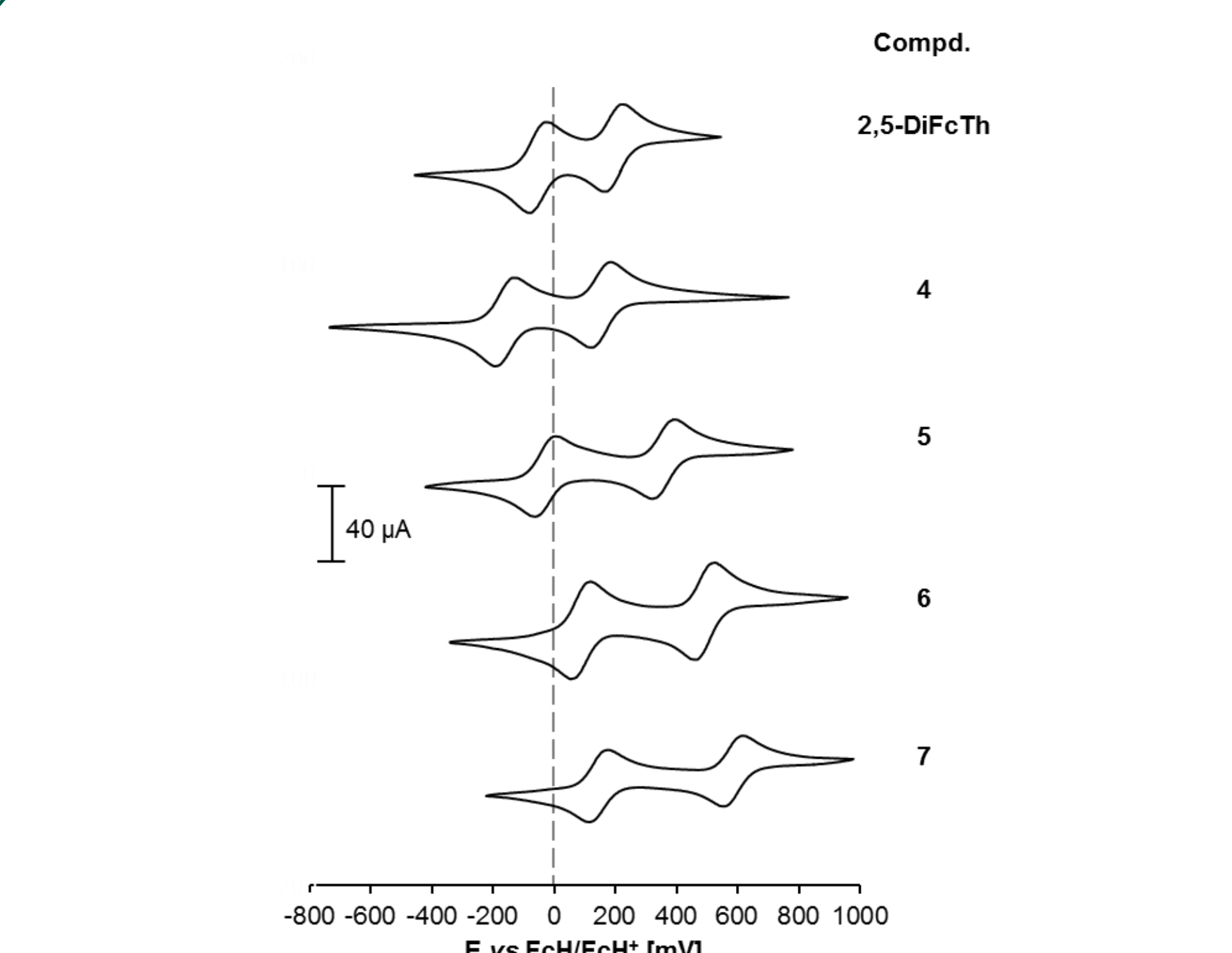
## Solid state structure

➡ Compound **3** crystallizes in the orthorhombic space group *P* 2<sub>1</sub>2<sub>1</sub>. The pyrrole is on a plain with the directly bonded cyclopentadienyls. The phenyl unit is vertical oriented to the pyrrole core. Features are the parallel oriented ferrocenyls and the formyl groups, which are vectored in the same direction.



**Figure 1:** Molecular structure of **3**. All hydrogen atoms and have been omitted for clarity.

## Electrochemistry



**Figure 2:** Cyclic voltammograms of **4** – **7** in dry dichloromethane (1 mM) 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 M). [2]

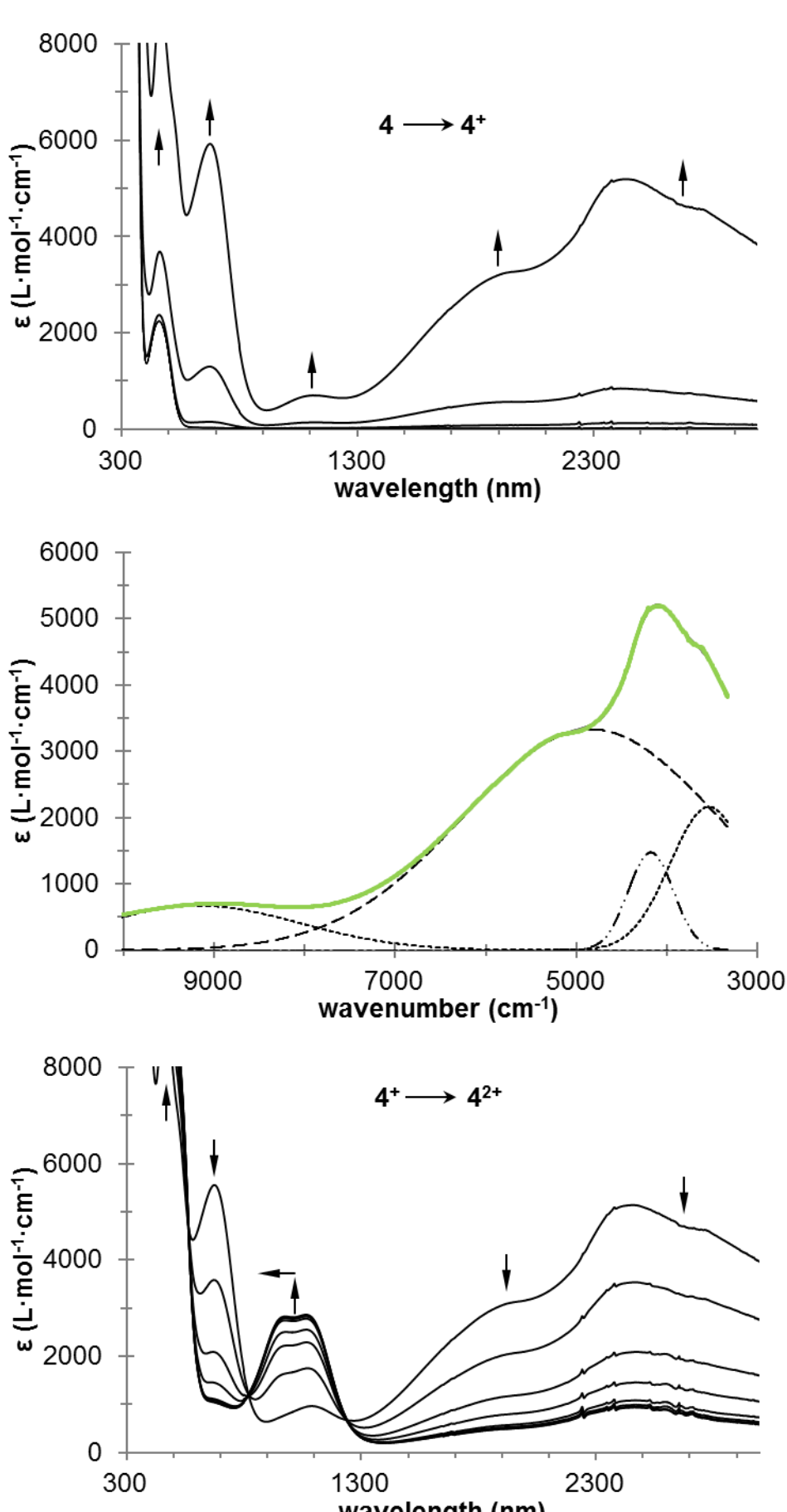
➡ Under our experimental conditions, the ferrocenyl thiophenes **4** – **7** display two well resolved electrochemically reversible one-electron transfer processes. In comparison with 2,5-diferrocenyl thiophene [2] (2,5-DiFcTh), the additional ethylene dioxy bridge in **4** leads to a cathodic shift of the ferrocenyl redox potentials in combination with an increased redox separation. The installation of further electron withdrawing substituents on the ferrocenyl units results also in enlarged Δ*E*<sup>o</sup> values (**5** – **7**, Figure 2, Table 1). Such an increase of the redox separation between the ferrocenyls suggests a higher degree of electronic interaction. The spectroelectrochemical studies reveal increasing metal-metal interactions in the mixed-valent species due to donor groups on the thiophene as well as acceptor-substituted ferrocenyl units (Table 3, Figure 4).

**Table 3:** NIR data, regarding IVCT absorptions of **4**<sup>+</sup> and **7**<sup>+</sup>. [2]

Compd.	$\nu_{max}$ [cm <sup>-1</sup> ] ( $\epsilon_{max}$ [L·mol <sup>-1</sup> ·cm <sup>-1</sup> ])	$\Delta\nu_{1/2}$ [cm <sup>-1</sup> ] ( $\Delta\nu_{1/2(theo)} = (2310\nu_{max})^{1/2}$ )
(2,5-DiFcTh) <sup>+</sup>	4990 (2130)	3840
<b>4</b> <sup>+</sup>	4840 (3330)	3300
<b>7</b> <sup>+</sup>	4780 (3930)	3080

**Table 1:** Cyclic voltammetric data (E vs FcH/FcH<sup>+</sup>) of **4** – **7** (1 mM) in dichloromethane, [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.1 M) at 25 °C. [2]

Compd.	$E^o/\Delta E_p/\Delta E^o$ [mV]	
	Wave (no.)	
	(1)	(2)
2,5-DiFcTh	-53/60	195/62/248
4	-160/64	153/66/313
5	-29/66	369/69/388
6	90/69	493/73/403
7	145/62	586/63/441



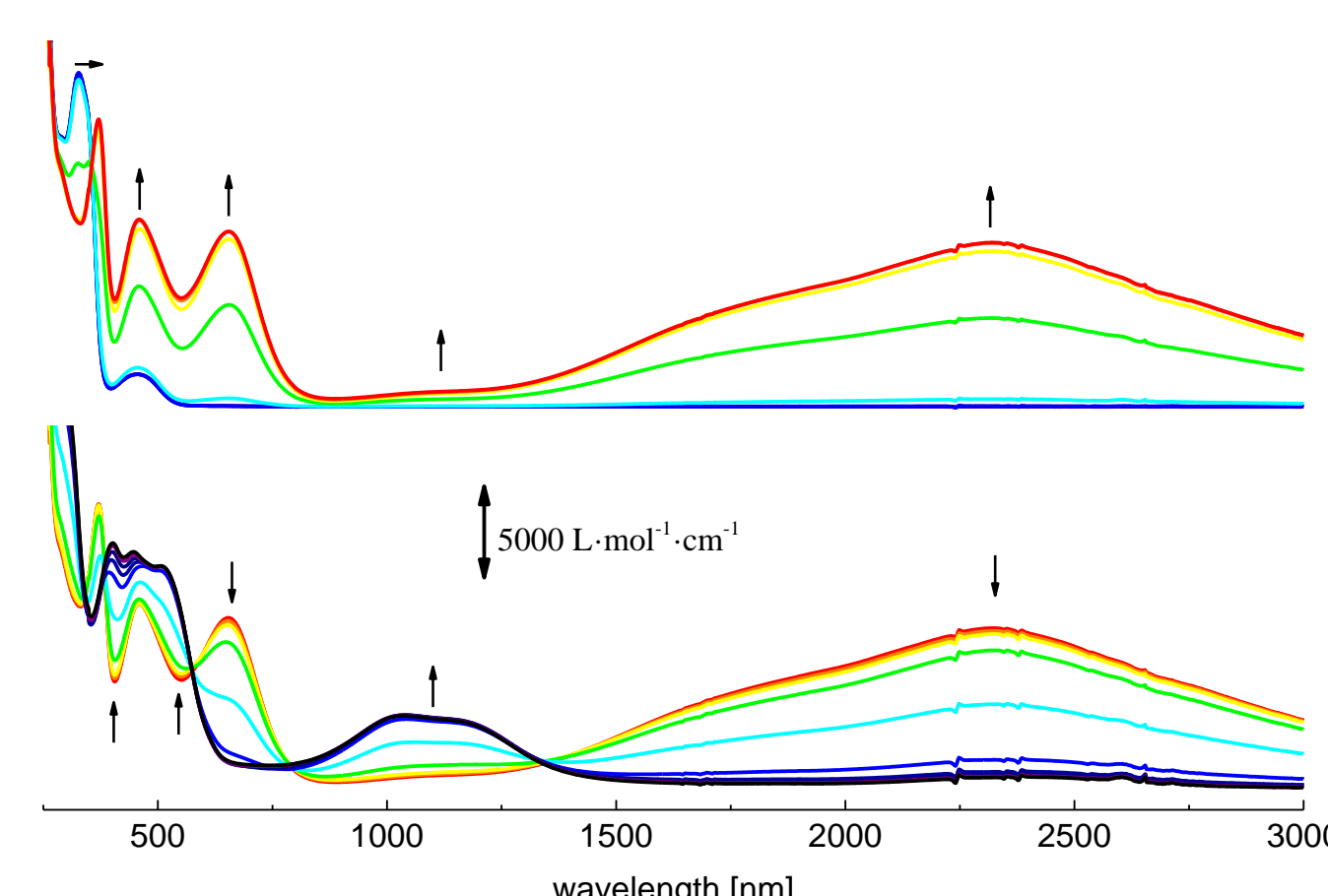
**Figure 4:** UV-Vis/NIR spectra of **4** at rising potentials. Middle: deconvolution of NIR absorptions at 300 mV, four Gaussian shaped transitions (dashed line: IVCT; dotted line: LMCT/MLCT; dotted dashed line: LF. Arrows indicate increasing or decreasing as well as shifting absorptions.

**Table 2:** Cyclic voltammetric data (E vs FcH/FcH<sup>+</sup>) of **1** – **3** (1 mM) in dichloromethane, [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.1 M) at 25 °C. [2]

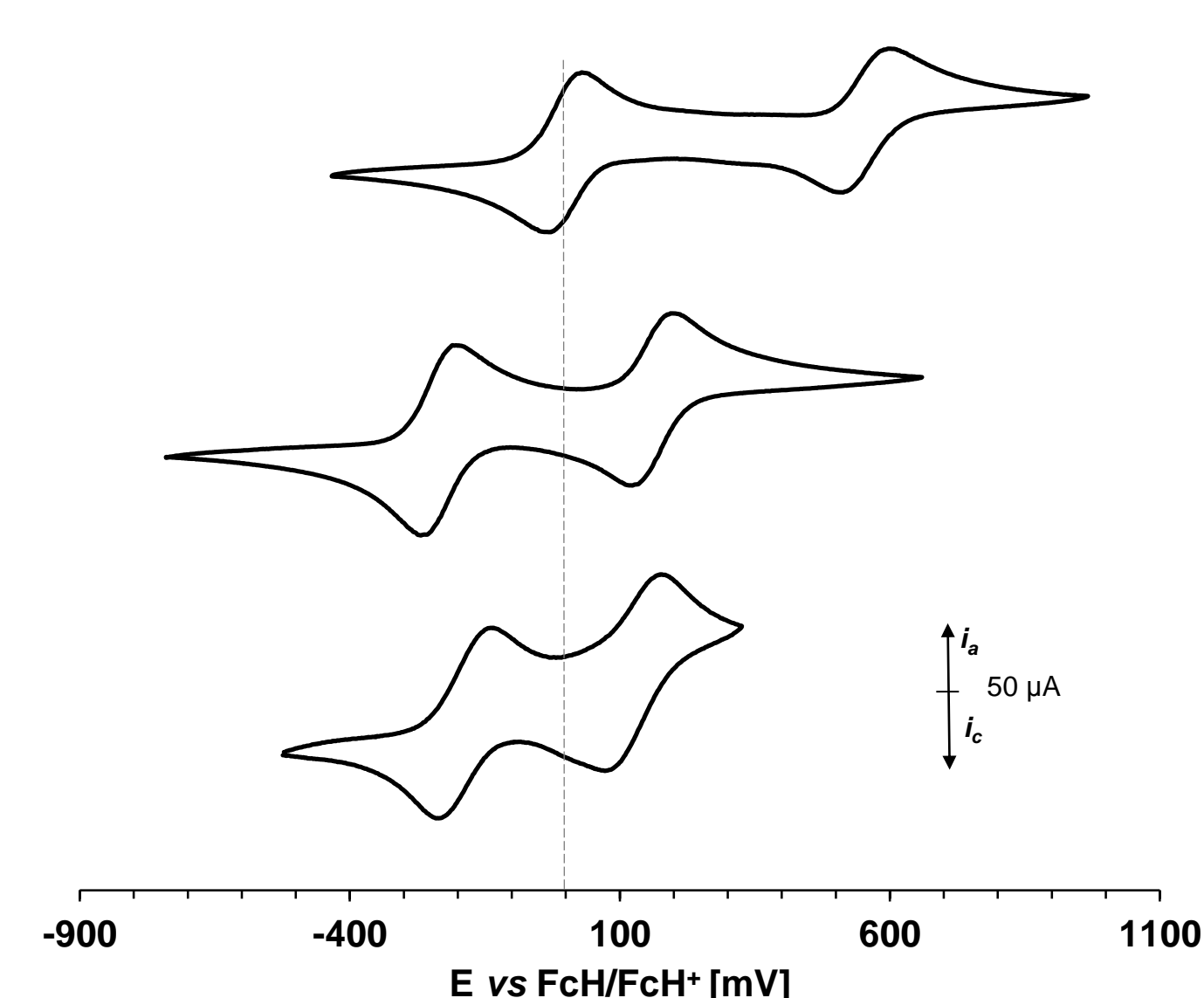
Compd.	$E^o/\Delta E_p/\Delta E^o$ [mV]	
	Wave (no.)	
	(1)	(2)
<b>2</b>	-235/66	158/77/393
<b>1</b>	-238/68	212/75/450
<b>3</b>	1/64	554/91/553

➡ In Figure 3 cyclic voltammograms of the synthesized pyrroles are shown. Two reversible one-electron transfer processes are characteristic. The electron withdrawing effect of the formyl groups in **3** induces a large redox separation of 553 mV.

➡ Spectroelectrochemical studies of the pyrroles were performed by stepwise increasing the potentials from -500 to 1200 mV vs Ag/AgCl in an OTTE cell using [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte. This allows an oxidation of the analytes to form monocationic- and dicationic species. As representative example NIR absorptions of compound **2** during oxidation are pictured (Figure 5).

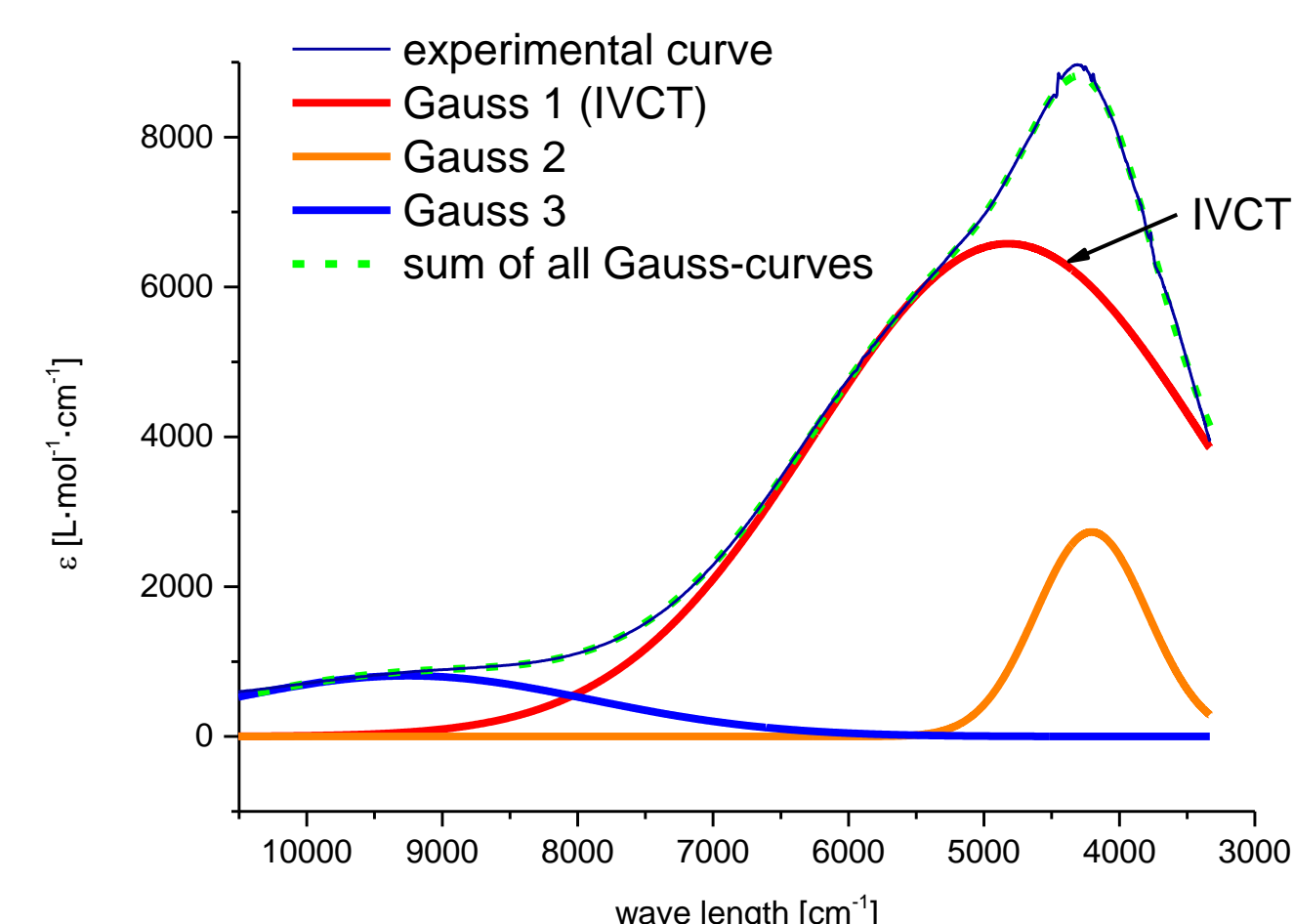


**Figure 5:** UV-Vis/NIR spectra of **2** at rising potentials (top: -200-225 mV, bottom: 250-650 mV) v.s. Ag/AgCl.



**Figure 3:** Cyclic voltammograms of **3** (top), **2** (middle) and **1** (down). [2]

➡ To characterize the NIR absorption bands of the mixed-valent species gauss-deconvolution was done, using three Gauss shaped absorptions (Figure 6). For **2**<sup>+</sup> an IVCT band at 4830 cm<sup>-1</sup> with an intense absorption (ε = 6580 L·mol<sup>-1</sup>·cm<sup>-1</sup>) was found. Compound **3**<sup>+</sup> shows an IVCT band at 5240 cm<sup>-1</sup> with an extinction of 5440 L·mol<sup>-1</sup>·cm<sup>-1</sup>. Thus, these experimental data reveal increasing electronic interactions between the iron centers in the intervalent species by electron acceptor substituents on the ferrocenyl moieties.



**Figure 6:** Deconvolution of the NIR spectra of **2**<sup>+</sup>.

## Conclusion

The synthesis of diferrocenyl-substituted pyrrole and thiophene derivatives using palladium-promoted Negishi C,C couplings of 2,5-dibromoheterocycles and corresponding organozinc compounds is reported. The obtained diferrocenyl pyrroles and thiophenes were analyzed using electrochemical methods. These studies reveal increasing metal-metal interactions in the corresponding mixed-valent species due to acceptor substituents on the ferrocenyl units. It could also be shown that the interaction between the iron centers becomes stronger with electron donor functionalities on the heterocyclic core.

## References and Acknowledgement

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