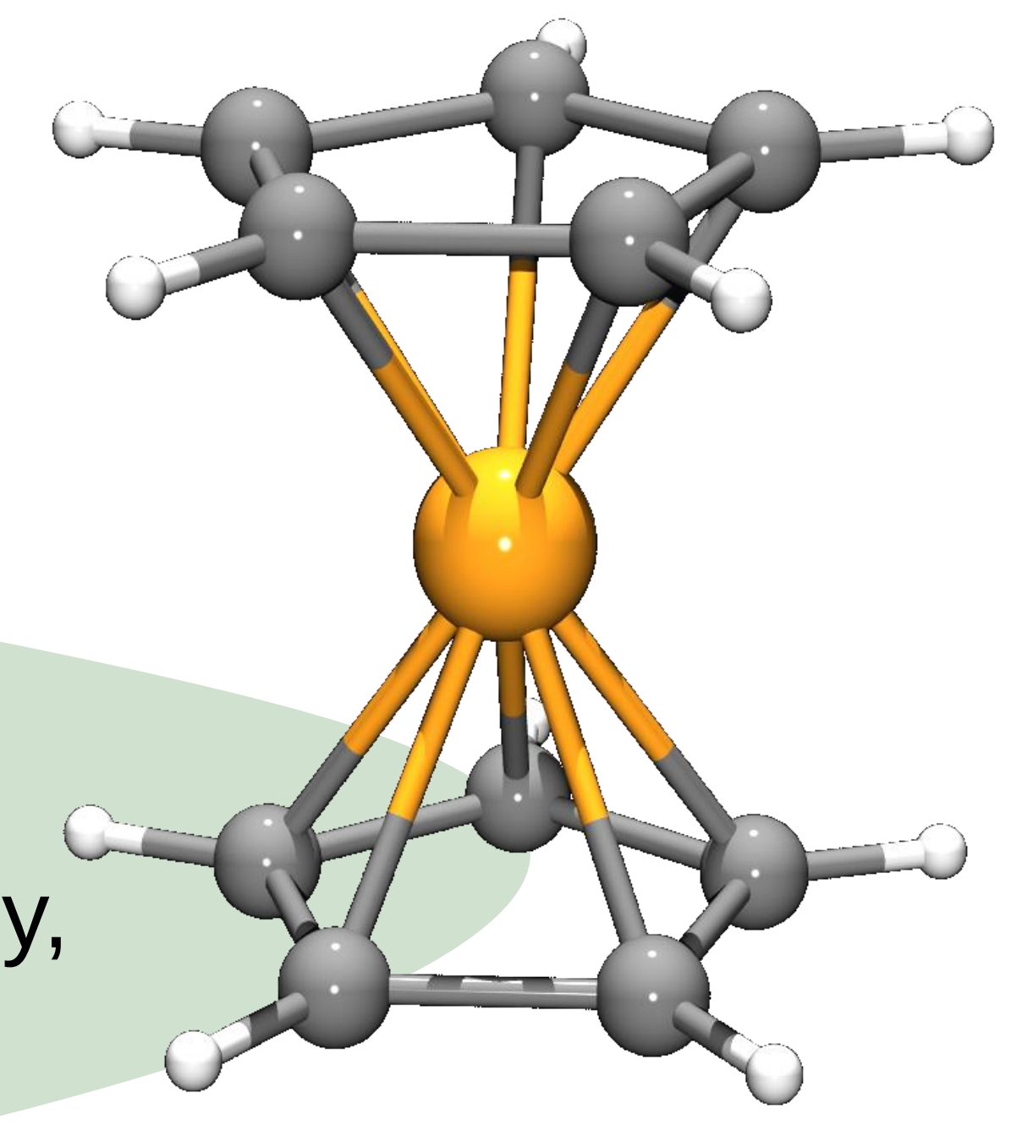
Electrochemical behavior of modified phenyl substituents at a biferrocene backbone

Qing YUAN, Dominique MIESEL, Alexander HILDEBRANDT, Matthäus SPECK and Heinrich LANG*

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry,
Inorganic Chemistry, D-09107 Chemnitz, Germany
qing.yuan@s2011.tu-chemnitz.de



Introduction and Motivation

Biferrocene is commonly used as a model compound for investigating mixed-valent species, due to the chemical stability of its oxidized form and the electrochemical reversibility between its oxidized and neutral species.[1,2] Although it is known that electron-donating or –withdrawing groups are used to modify the effectivity of intervalence charge transfer (IVCT),[3,4] basic studies for biferrocene are pending .

Synthesis

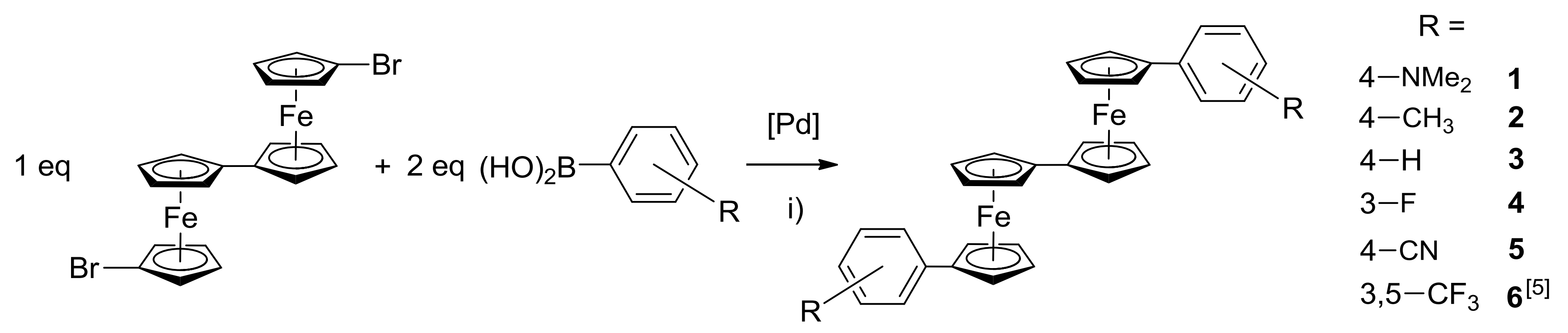


Figure 1. Synthesis of compounds **1-6** via Suzuki Miyaura *C*,*C* cross-coupling: i) 4 mol-% [Pd]= [Pd(dppf)Cl$_2$], $K_3PO_4 \cdot H_2O$, toluene or tetrahydrofuran, 80 °C.

Electrochemistry

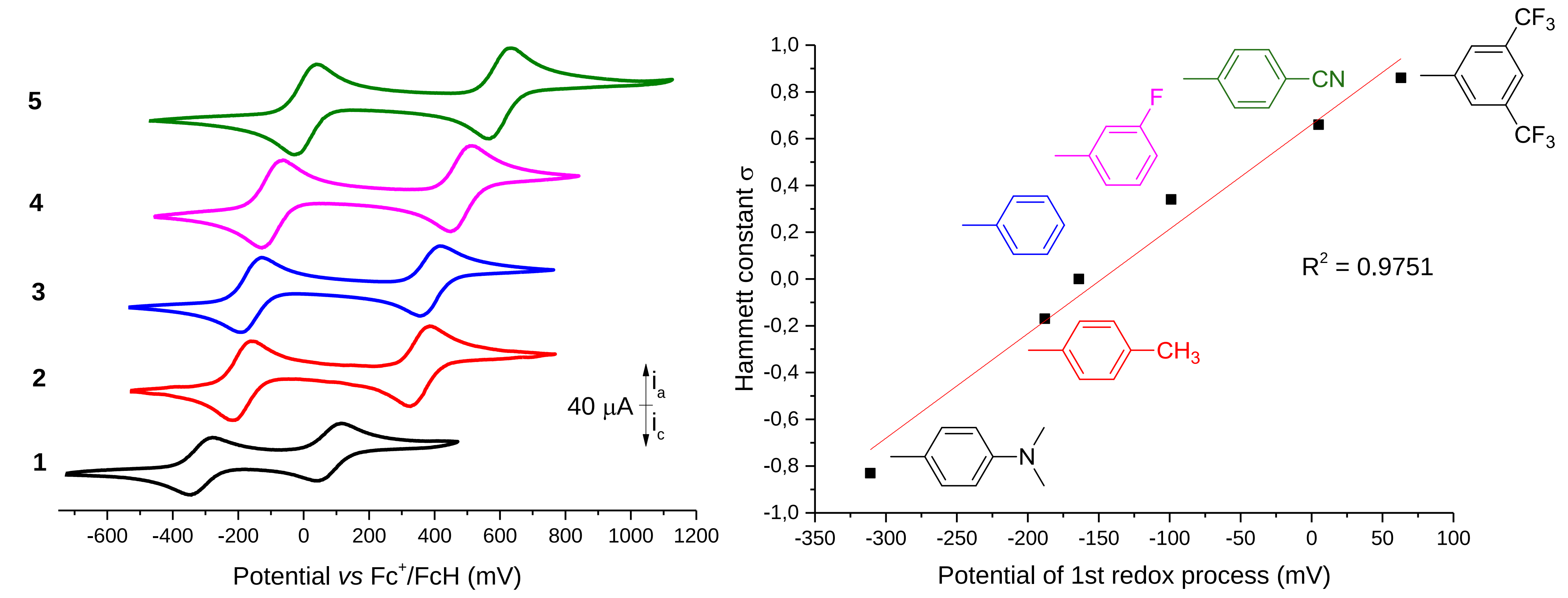


Figure 2. Cyclic voltammograms (CV) (left), correlation of the 1st redox potentials and the Hammett constants σ (right) of compounds **1-6** in dichloromethane solutions (1.0 mmol·L^{-1}) at 25 °C; scan rate 100 mV·s^{-1}; supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol·L^{-1}).

Table 1. CV Data of compounds **1-6**

	[N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$]			**[N^{n}Bu$_4$]PF$_6$**	$\Delta\Delta E^{\circ\prime}$
	$E_1^{\circ\prime}$ (mV)	$E_2^{\circ\prime}$ (mV)	$\Delta E^{\circ\prime}$ (mV)	$\Delta E^{\circ\prime}$ (mV)	(mV)
1	-311	77	388	281	107
2	-188	355	543	362	181
3	-164	386	550	360	190
4	-99	440	539	375	164
5	5	560	555	373	182
6[5]	63	683	620	380	240

Conditions of measurements: [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] or [N^{n}Bu$_4$]PF$_6$ as supporting electrolytes (0.1 mol·L^{-1}) in dichloromethane solutions (1.0 mmol·L^{-1}) at 25 °C; scan rate 100 mV·s^{-1}

Spectroelectrochemistry

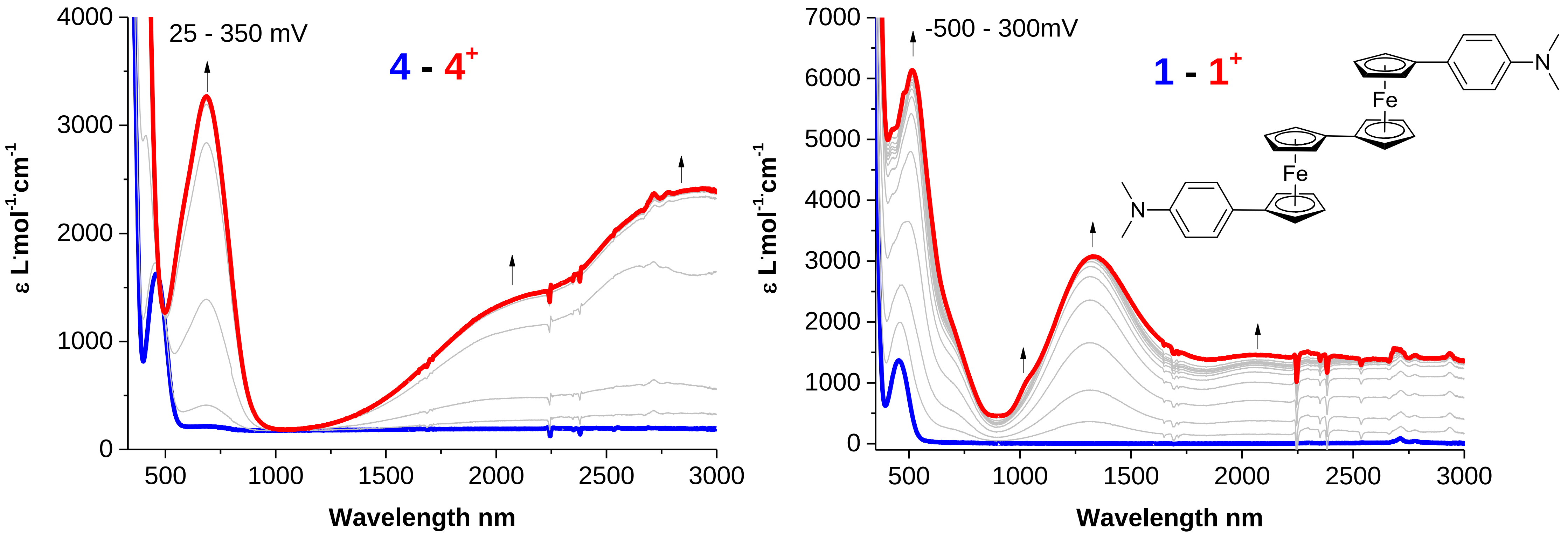


Figure 3. UV-Vis/NIR spectra of compounds **4** (left) and **1** (right), generated in an OTLLE (Optically Transparent Thin Layer Electrochemical) cell in dichloromethane solutions (2.0 mmol·L^{-1}) at 25 °C; supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol·L^{-1}).

Table 2. IVCT band properties of oxidized species **1$^+$-6$^+$**.

	v_{max} (cm^{-1}) (ε (L·mol^{-1}·cm^{-1}))	**$\Delta v_{1/2}$ (cm^{-1})**	**$\Delta v_{1/2theo.}$^{a} (cm^{-1})**
1$^+$	5132 (896)	3075	3443
2$^+$	5040 (1228)	3300	2761
3$^+$	4545 (1195)	2819	3240
4$^+$	4461 (1415)	3121	2802
5$^+$	4454 (955)	2901	2793
6$^+$[5]	4429 (1528)	2903	3198

Conditions of measurements: generated in an OTLLE (Optically Transparent Thin Layer Electrochemical) cell in dichloromethane solutions (2.0 mmol·L^{-1}) at 25 °C; supporting electrolyte [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol·L^{-1}).

[a]: Values calculated as $\Delta v_{1/2theo} = (2320 \cdot v_{max})^{1/2}$ according to the Hush relationship for week coupling systems.[6]

Spectroelectrochemical studies show that the generated mono-oxidized species **1$^+$-6$^+$** possess broad IVCT absorptions in the NIR (near Infrared) region. The bands are shifted to lower energy, while increasing the electron-donating character of the substituents from 4430 cm^{-1} to 5100 cm^{-1}. Compounds **2$^+$-6$^+$** exhibit a similar absorption behavior (Figure 3. left). In contrast to them, mono-cationic **1$^+$** shows an additional strong absorption band at 1400 nm, due to the redox-active amino groups.

Conclusion

- CV investigations showed an increase of the 1st redox potential due to the enhanced electron-withdrawing character of the functionality.
- UV-Vis/NIR spectroelectrochemistry studies demonstrated that an electron-donating group can decrease the energie for IVCT.
- An additional charge transfer between a redox-active substituent and iron could be observed.

References and Acknowledgement

[1] D. O. Cowan, F. Kaufman, *J. Am. Chem. Soc.* **1970**, *92*, 219–220.
[2] C. Levanda, K. Bechgaard, D. Cowan, *J. Org. Chem.* **1976**, *41*, 2700–2704.
[3] A. Hildebrandt, H. Lang, *Dalton Trans.* **2011**, *40*, 11831–11837.
[4] M. Lohan, H. Lang, *Organometallics* **2010**, *29*, 4804–4817.
[5] J. M. Speck, *Dissertation: Ferrocenyl-substituted Thiophenes – Electrochemical Behavior and Charge Transfer,* **2016**, TU Chemnitz
[6] N. S. Hush, *Prog. Inorg. Chem.* **1967**, 391–444.