The influence of electron withdrawing and -donating functionalities on the electron transfer properties in substituted biferrocenes

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Introduction

Electron transfer (ET) within the mixed-valent complexes has attracted scientific attention during recent years.[1] Within the work presented here, the effect of variant electron density at the iron atoms on the ET within substituted biferrocenes is investigated. Biferrocenes have been among the first mixed valent species and thus have been thoroughly studied. While steric influences on the electron transfer properties are well described, a systemic analysis of electronic changes within mixed-valent biferrocenes has not been documented this far.

Synthesis

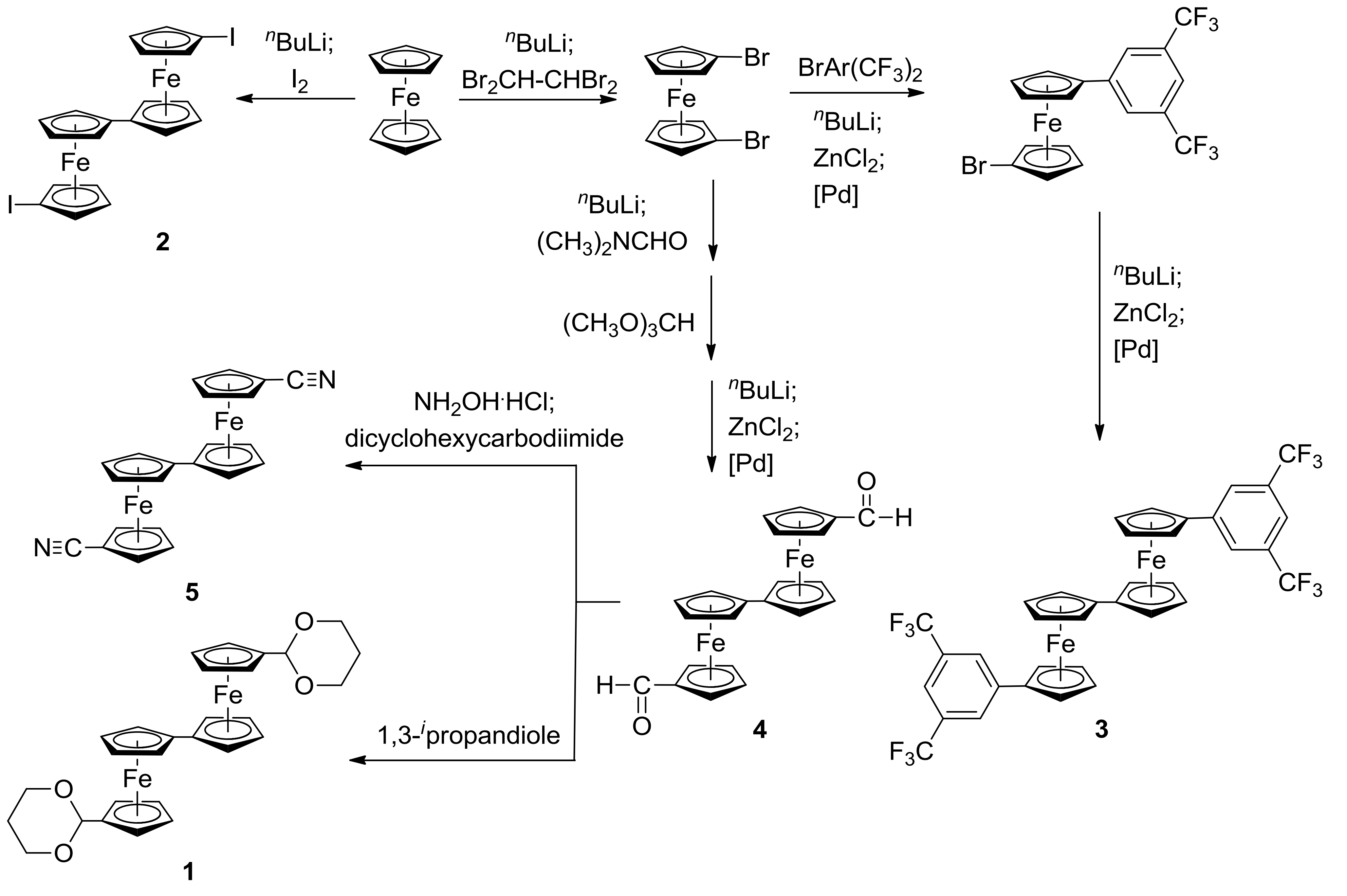

Figure 1: Synthesis of compounds **1 - 5**. ([Pd] = $[Pd(CH_2CMe_2P^tBu_2)(\mu\text{-}Cl)]_2$)

In this work, a serie of substituted biferrocenes **1** - **5** was studied. Compound **3** and **4** were synthesized stepwisely by a palladium-catalyzed Negishi *C,C*-cross coupling reaction from dibromoferrocene, while diacetal- (**1**) and dicyano-substituted biferrocene (**5**) were prepared in a one-step reaction from **4**, respectively. Diiodobiferrocene (**2**) was obtained from the iodation of ferrocene.

The electron transfer properties of this serie of molecules were studied by electro- (CV - SWV) and spectroelectrochemistry (*in-situ* UV/Vis/NIR measurements).

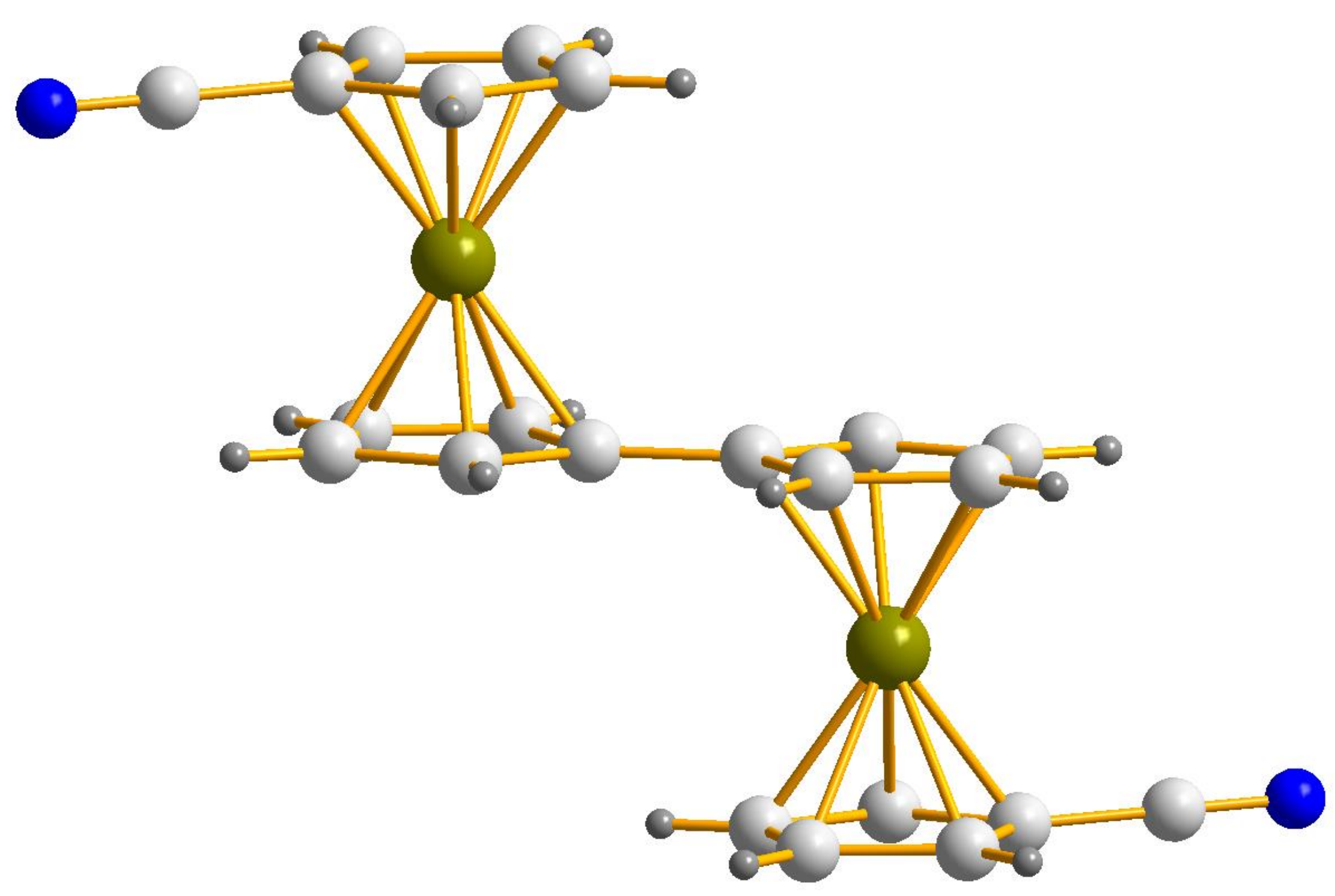

Figure 2: Solid-state-structur of compound **5**.

(Spectro)Electrochemistry

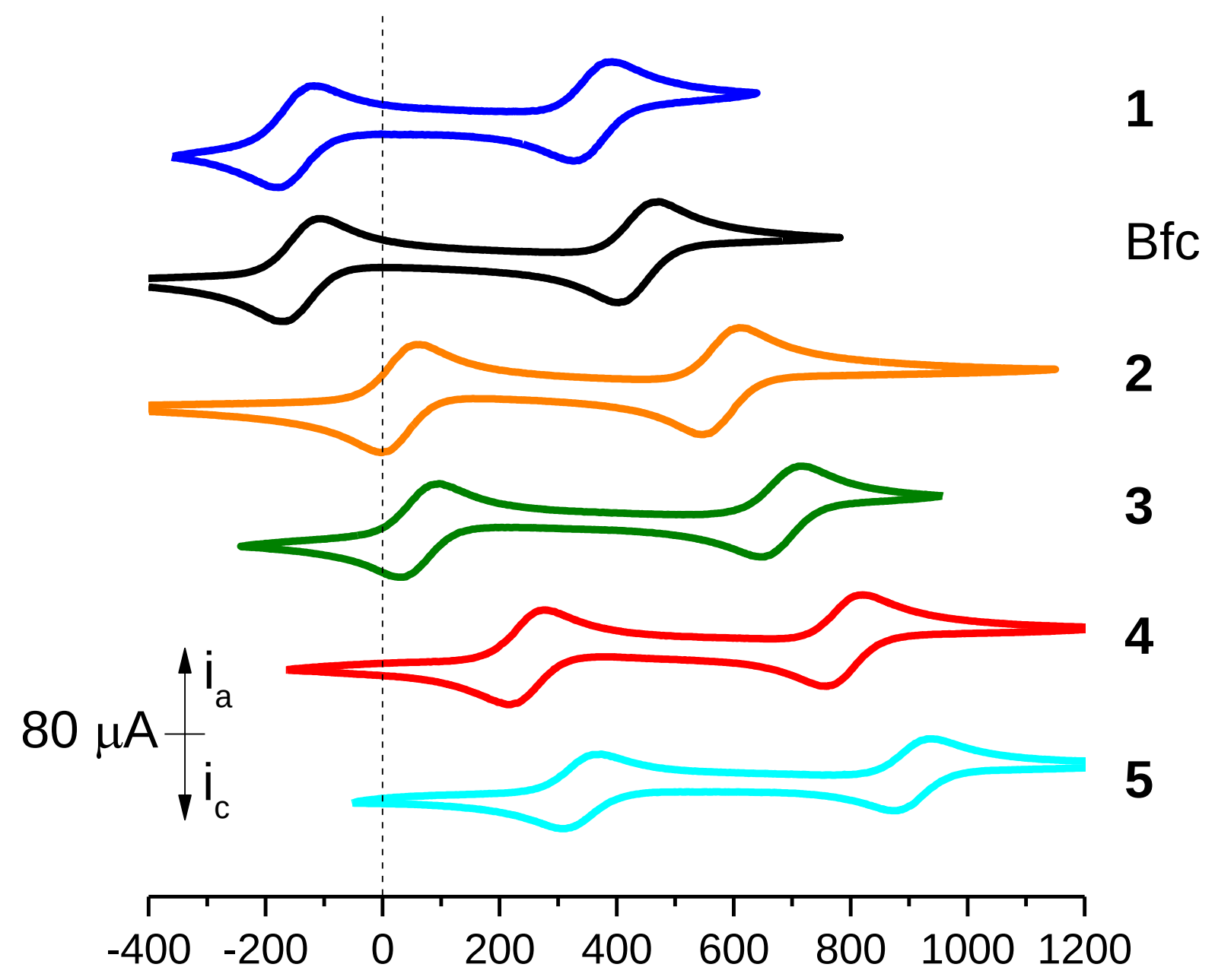

Figure 3: Cyclic voltammograms (CV) of compounds **1** - **5** and Bfc with an analytic concentration of 1 mM in CH_2Cl_2 containing 0.1 M $N(^nBu)_4[B(C_6F_5)_4]$ at 25 °C

Compound	$N(^nBu)_4[B(C_6F_5)_4]$ $E_1^{\circ\prime}$ ($\Delta E_p^{\circ\prime}$) (mV)	$E_2^{\circ\prime}$ ($\Delta E_p^{\circ\prime}$) (mV)	$\Delta E^{\circ\prime}_{[B(C_6F_5)_4]^-}$ (mV)	$N(^nBu)_4PF_6$ $\Delta E^{\circ\prime}_{PF_6^-}$ (mV)	$\Delta\Delta E^{\circ\prime}$ (mV)[a]
1	-150 (58)	355 (61)	505	–	–
Bfc[2]	-137 (62)	436 (64)	570	375	192
2	25 (58)	580 (58)	555	380	175
3	63 (64)	683 (69)	620	380	240
4	245 (60)	795 (60)	550	325	225
5	338 (62)	908 (62)	570	350	220

[a]: $\Delta\Delta E^{\circ\prime} = \Delta E^{\circ\prime}_{[B(C_6F_5)_4]^-} - \Delta E^{\circ\prime}_{PF_6^-}$

Tabel 1: CV Data of compounds **1** - **5** and Bfc with an analytic concentration of 1 mM in CH_2Cl_2 containing 0.1 M $N(^nBu)_4[B(C_6F_5)_4]$ and $N(^nBu)_4PF_6$, respectively, at 25 °C

Within the electrochemical measurements, the effect of the electron withdrawing functionalities on the electron density at the ironatoms is reflected by an anodic shift of the 1st ferrocene based redox potential. Further more measurements in different electrolytes allowed for the evaluation of electrostatic stabilization effects of the mixed valent complexes **1**$^+$ - **5**$^+$ ($\Delta\Delta E^{\circ\prime}$). The $\Delta\Delta E^{\circ\prime}$ values showed that the electrostatic repulsion in electron poor **4**$^+$ and **5**$^+$ is more pronounced than in the iodo derivative **2**$^+$.

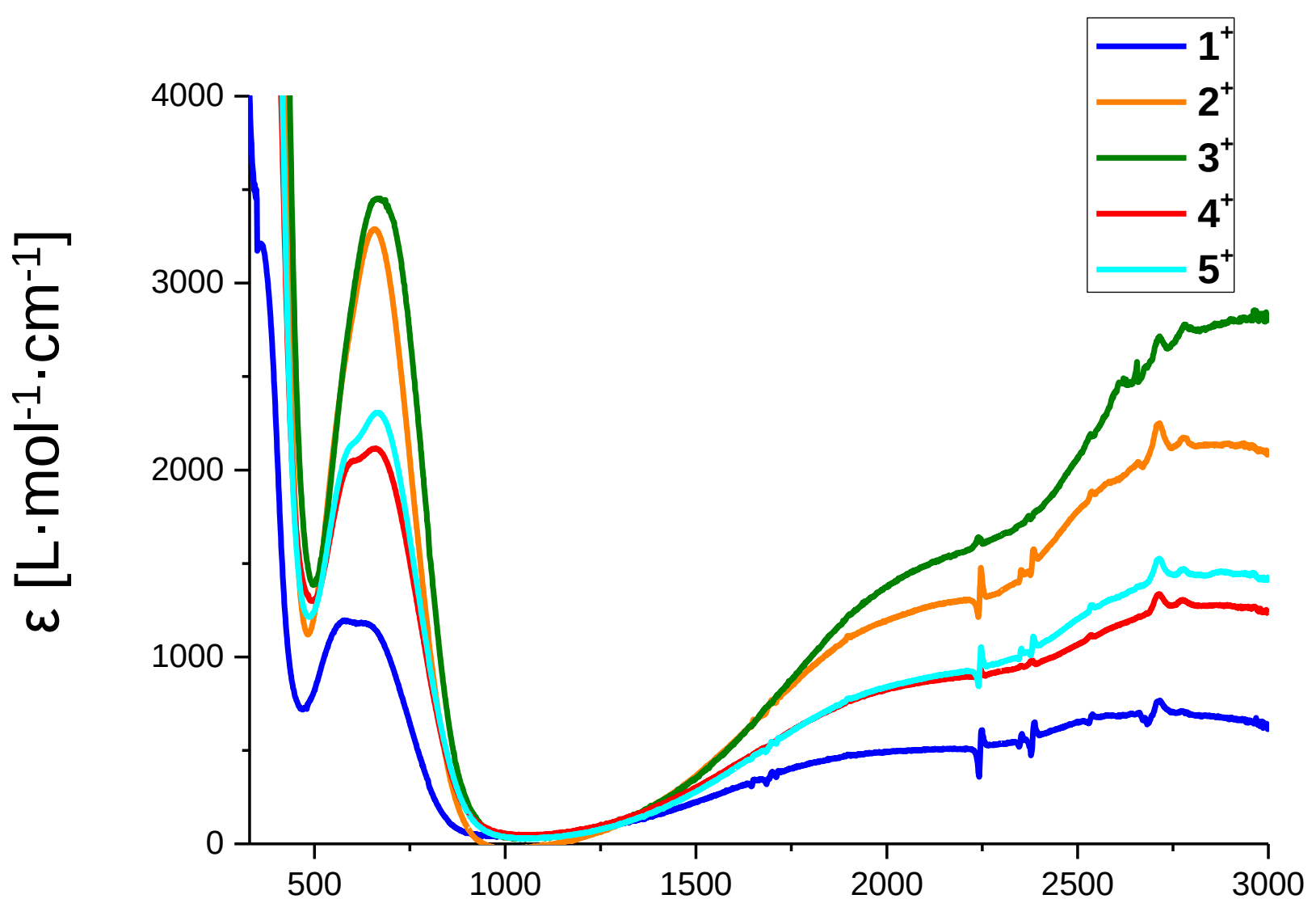

Figure 4: UV/Vis/NIR-Spektra of species **1**$^+$ - **5**$^+$.

Compound	$\tilde{\nu}_{max}$ (cm^{-1}) (ε_{max} (L·mol^{-1}·cm^{-1}))	$\Delta\tilde{\nu}_{1/2}$ (cm^{-1})	$f \cdot 10^3$ (cm^{-1})	$\tilde{\nu}_{maxPC}$ - $\tilde{\nu}_{maxDCM}$
1$^+$	4765 (494)	3503	7.96	668
Bfc$^+$[2]	4400 (1360)	3510	21.96	1100
2$^+$	4559 (1258)	3104	17.96	–
3$^+$	4429 (1528)	2903	20.40	395
4$^+$	4414 (886)	3546	14.46	1085
5$^+$	4451 (899)	3353	13.87	1066

Tabel 2: Data of UV/Vis/NIR-Spektra for species **1**$^+$ - **5**$^+$ in dichlormethane and the shifts of the IVCT bands in propylencarbonate (PC) related to Bfc$^+$.

The oscillator strength of the IVCT bands of species **3**$^+$ - **5**$^+$ decreased with rising electron withdrawing ability. However, the significant low intensity of the IVCT band of species **1**$^+$ has been observed. Due to the poor solubility of iodobiferrocene in PC, its IVCT band was not be obtained.

Conclusion

In this work, the influences of functionalities in biferrocenes have been studied through electrochemical analysis.
The ET within biferrocenes system could be influenced by electron withdrawing or donating functionalities. In general, the trend could be observed that the electron transfer interactions decrease with increasing electron withdrawing character of the substituents, while the electrostatic interactions increase.

Reference and Acknowledges

[1] A. Hildebrandt, H. Lang, *Organometallics* **2013**, *32*, 5640–5653; A. Hildebrandt, H. Lang, *Dalt. Trans.* **2011**, *40*, 11831–11837; S. W. Lehrich, A. Hildebrandt, M. Korb, H. Lang, *J. Organomet. Chem.* **2015**, *792*, 37–45.

[2] J. M. Speck, *Ferrocenyl-Substituted Thiophenes – Electrochemical Behavior and Charge Transfer*, Technische Universität Chemnitz, **2016**.