Multi-functionalized Ferrocenes: “Synthesis and Characterization”

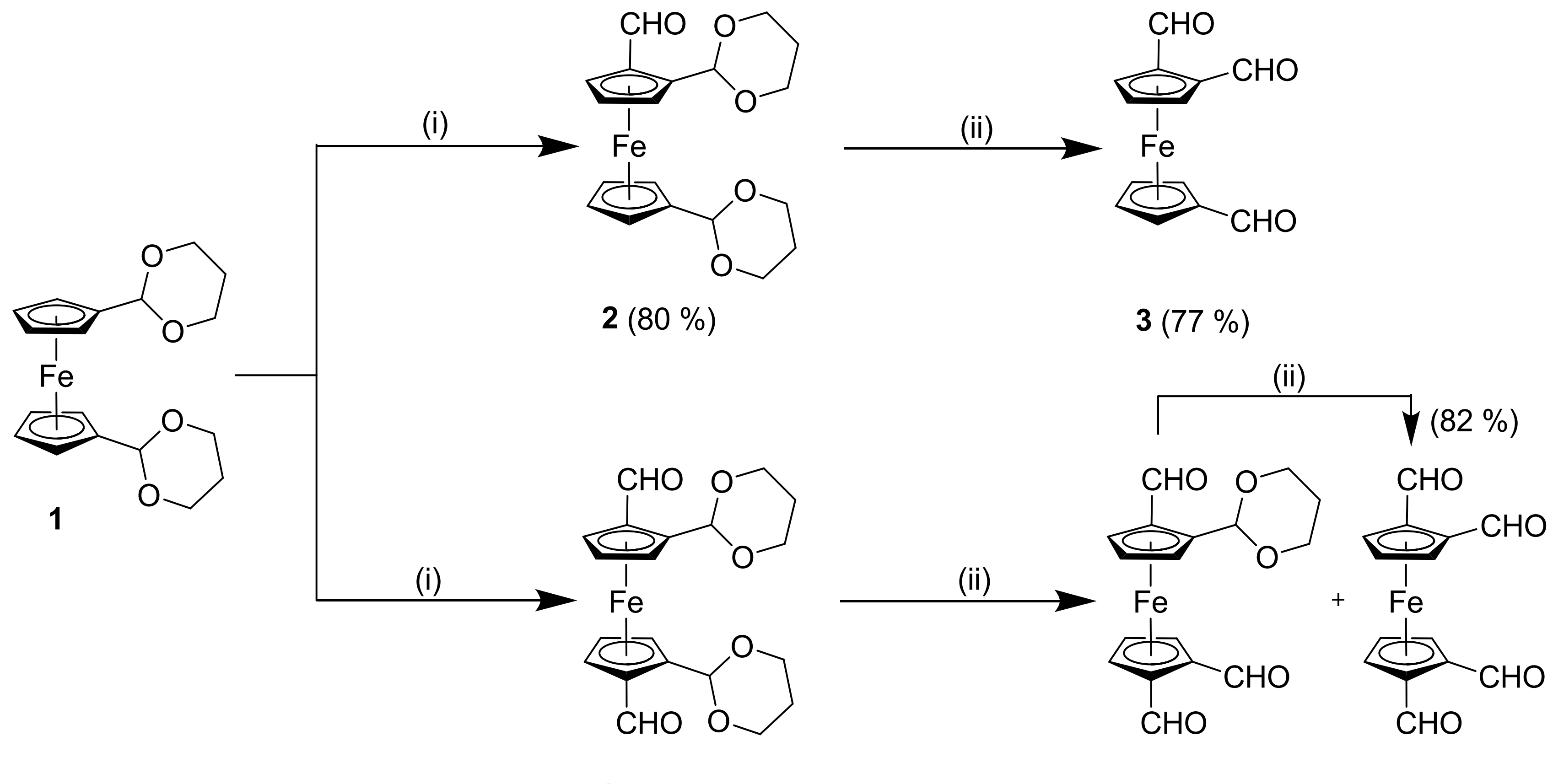
Khaled Al Khalyfeh, Alexander Hildebrandt*

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry,
Inorganic Chemistry, D-09107 Chemnitz, Germany
khaled-mohammad.al-khalyfeh@chemie.tu-chemnitz.de

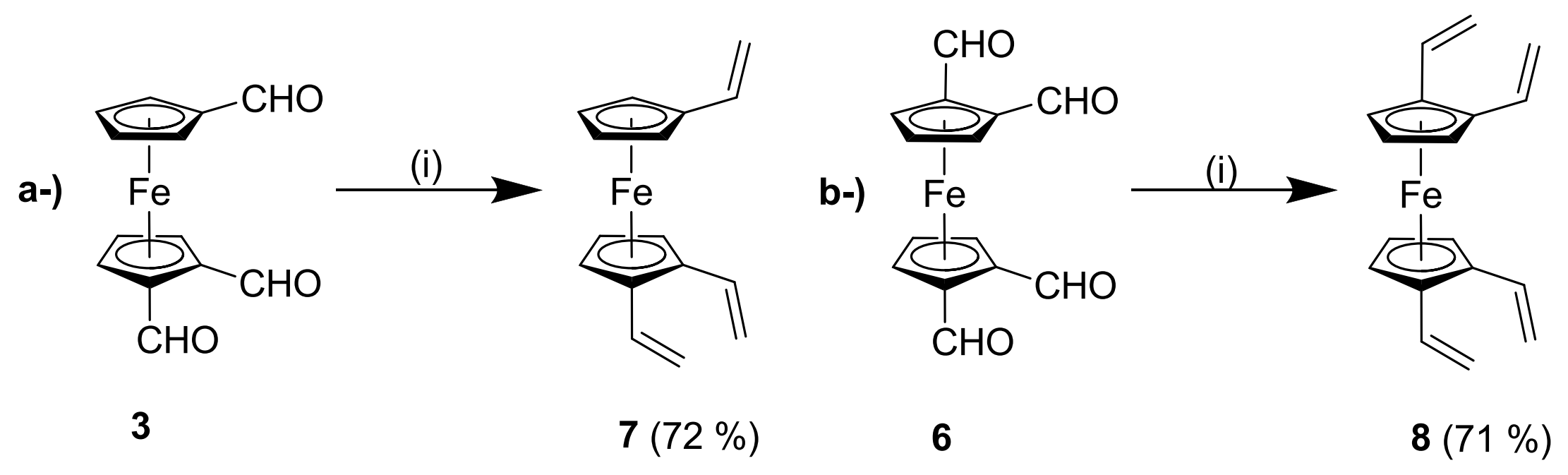
Introduction

One of the major advantages of ferrocenes is the possibility to introduce functional groups in a straightforward manner. For example, formyl-ferrocene and 1,1′-diformyl-ferrocene have proven to be valuable starting materials for the introduction of various functional groups at the ferrocene backbone.[1] Thereby, Wittig and Horner-Wadsworth-Emmons reactions allow their conversion into vinyl groups. Those vinyl-ferrocenes in turn have been used as starting material for the generation of ferrocenyl based conducting and semiconducting polymers.[2] Beside these applications of formyl-ferrocenes their electronic properties are also highly interesting. In this respect, a possibility to generate a ferrocenyl species with very high redox potential compared to ferrocene was achieved by the synthesis of formyl-ferrocenes bearing up to four formyl groups.[3]

Synthesis



Scheme 1. Formylation reaction of diacetal **1** forming aldehydes **2**–**6**; (i) 1st: ^{t}BuLi (1.1 equiv. for **2**; 2.2 equiv. for **4**), diethyl ether, –78 °C, 15 min; 2nd: 25 °C, 2 h; 3rd: dimethyl formamide (1.1 equiv. for **2**; 2.2 equiv. for **4**), –78 °C, 15 min; 4th: 25 °C, 2 h. (ii) trifluoromethanesulfonic acid, tetrahydrofuran, water, 25 °C, 24 h.



Scheme 2. Wittig reaction of aldehydes **3** and **6** forming vinyl ferrocenes **7** and **8**. (i) 1st: methyltriphenylphosphonium bromide (3.4 equiv. for **7**; 4.5 equiv. for **8**), tetrahydrofuran, 0 °C; 2nd: ^{n}BuLi (3.3 equiv. for **7**; 4.4 equiv. for **8**), 30 min; 3rd: 25 °C, 24 h.

X-ray Structure

Parallel displaced π ··· π interactions between two cyclopentadienyl rings are observed forming 1D chains along the a-axis where the Cp···Cp distances as short as 3.21Å. The aldehydic groups adopt as syn-periplanar conformation (α = 0 °) as well as the cyclopentadienyl carbons in both rings are eclipsed. Oxygen atoms of all aldehyde groups are directed to the opposing direction from each other.

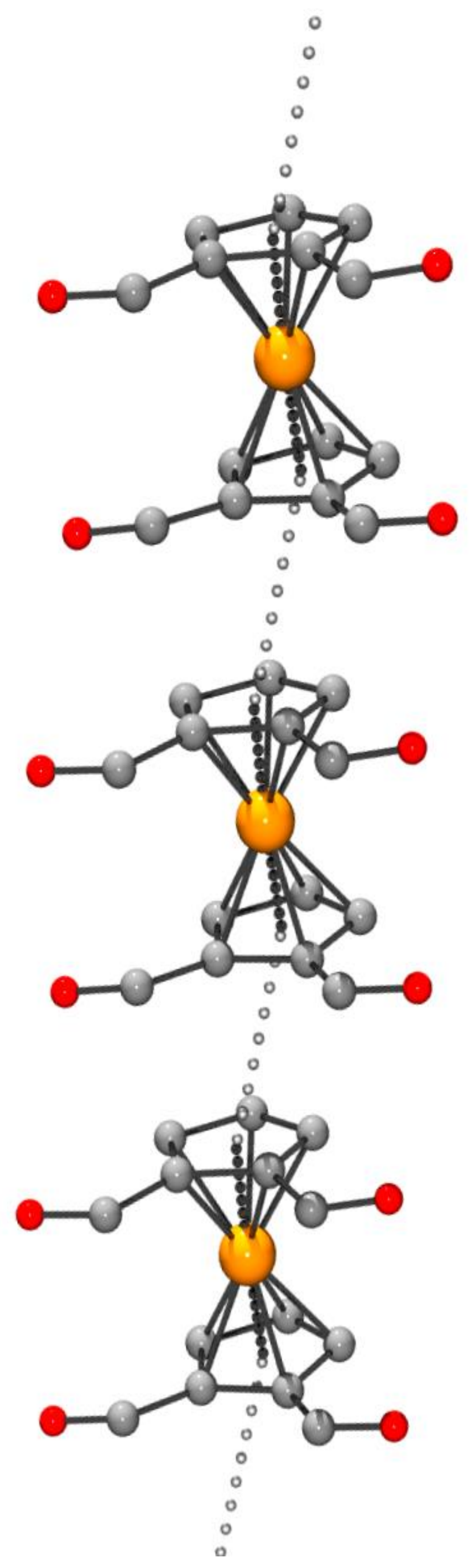
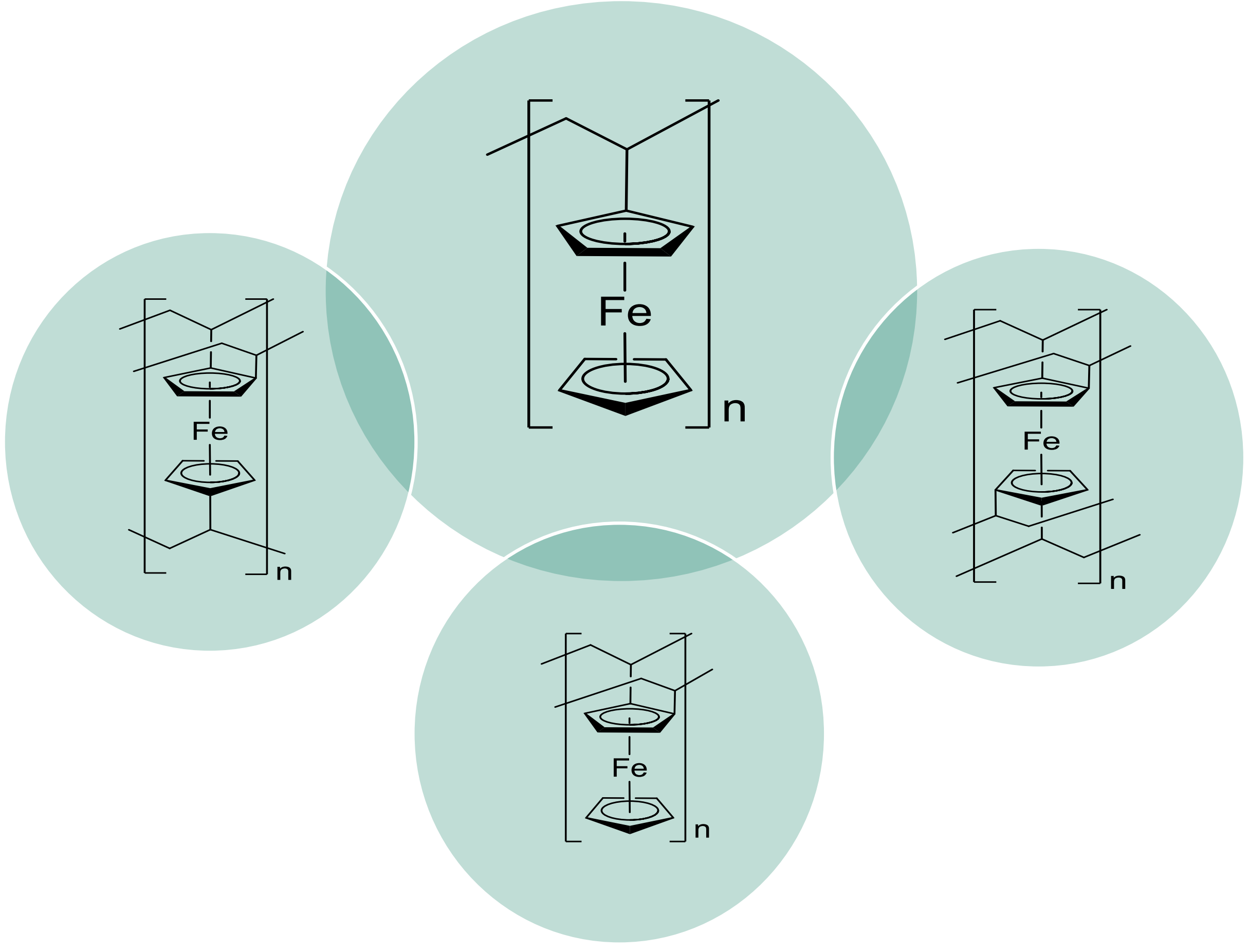


Figure 1. Graphical representation of the structure of compound **6** in the solid state.

Concept of Application

Cross Linking Polymers



Poly(vinylferrocenes) are in the focus recently as redox active polymers due to their chemical stability and high electrochemical reversibility. The copolymerization of vinylferrocenes with ferrocenes bearing two or more vinyl groups introduce additional cross linking to the polymer and hence alters the physical properties of the electro active material. For example, higher stability and elasticity are expected.

Electrochemistry

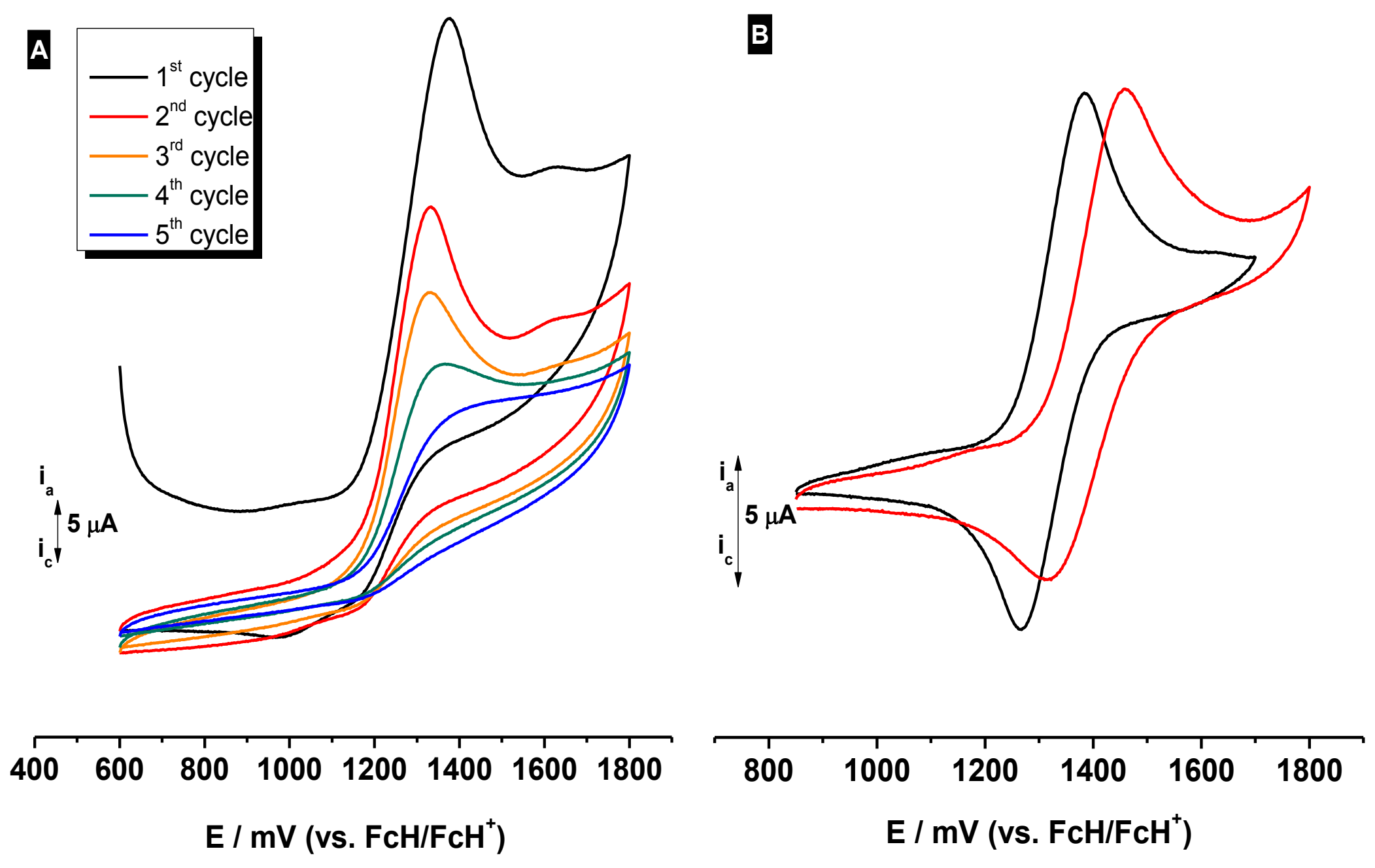


Figure 2. Cyclic voltammogram of **6** in dichloromethane; **A**: using $[N^{n}Bu_4][PF_6]$ (0.1 mol•L^{-1}) as supporting electrolyte. **B**: using $[N^{n}Bu_4][B(C_6F_5)_4]$ (0.1 mol•L^{-1}) as supporting electrolyte at 25 °C (red line) and –40 °C (black line).

Using of $[PF_6]^-$ within measurements of compound **6** resulted in an irreversible behavior which is most probably caused by deposition of the compound on the surface of the electrode, whereas, the lower ion-pairing capabilities of weakly coordinating $[B(C_6F_5)_4]^-$ minimize these deposition processes.[4] In addition cooling the samples down to –40 °C helped to prevent side reactions of the monocationic species and reversible redox processes have been observed.

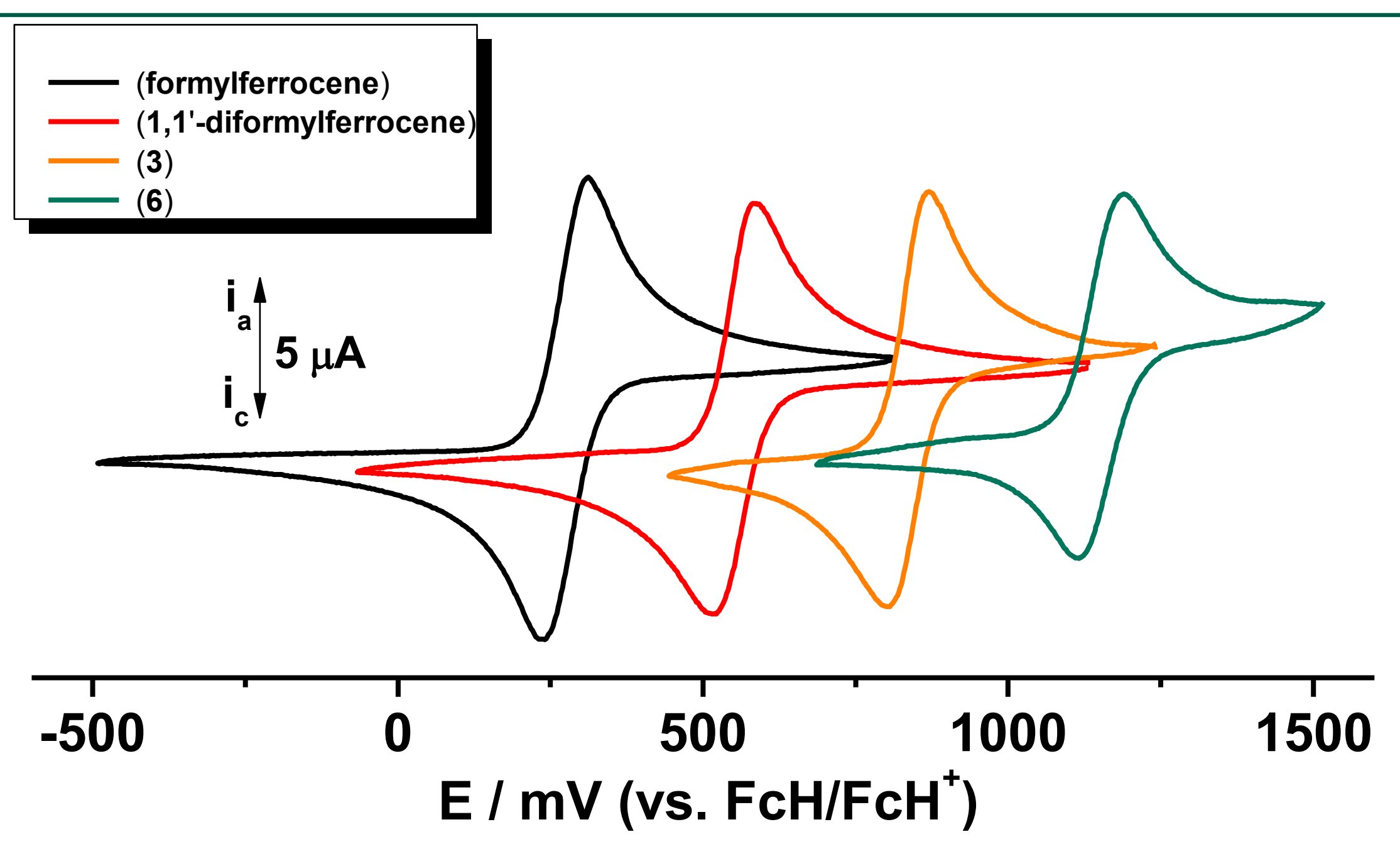


Figure 3. Cyclic voltammogram of formyl-, 1,1′-diformyl-ferrocene, **3** and **6** in DCM; 0.1 mol·L^{-1} $[N^{n}Bu_4][B(C_6F_5)_4]$ as supporting electrolyte at –40 °C.

The electron withdrawing effect of the formyl groups is reflected by the shift of $E°'$ towards higher potential. Within the series of ferrocenes bearing an increasing number of formyl groups (0 to 4) it can be shown that an additional aldehyde group will increase the redox potential of the appropriate compound by approximately 300 mV.

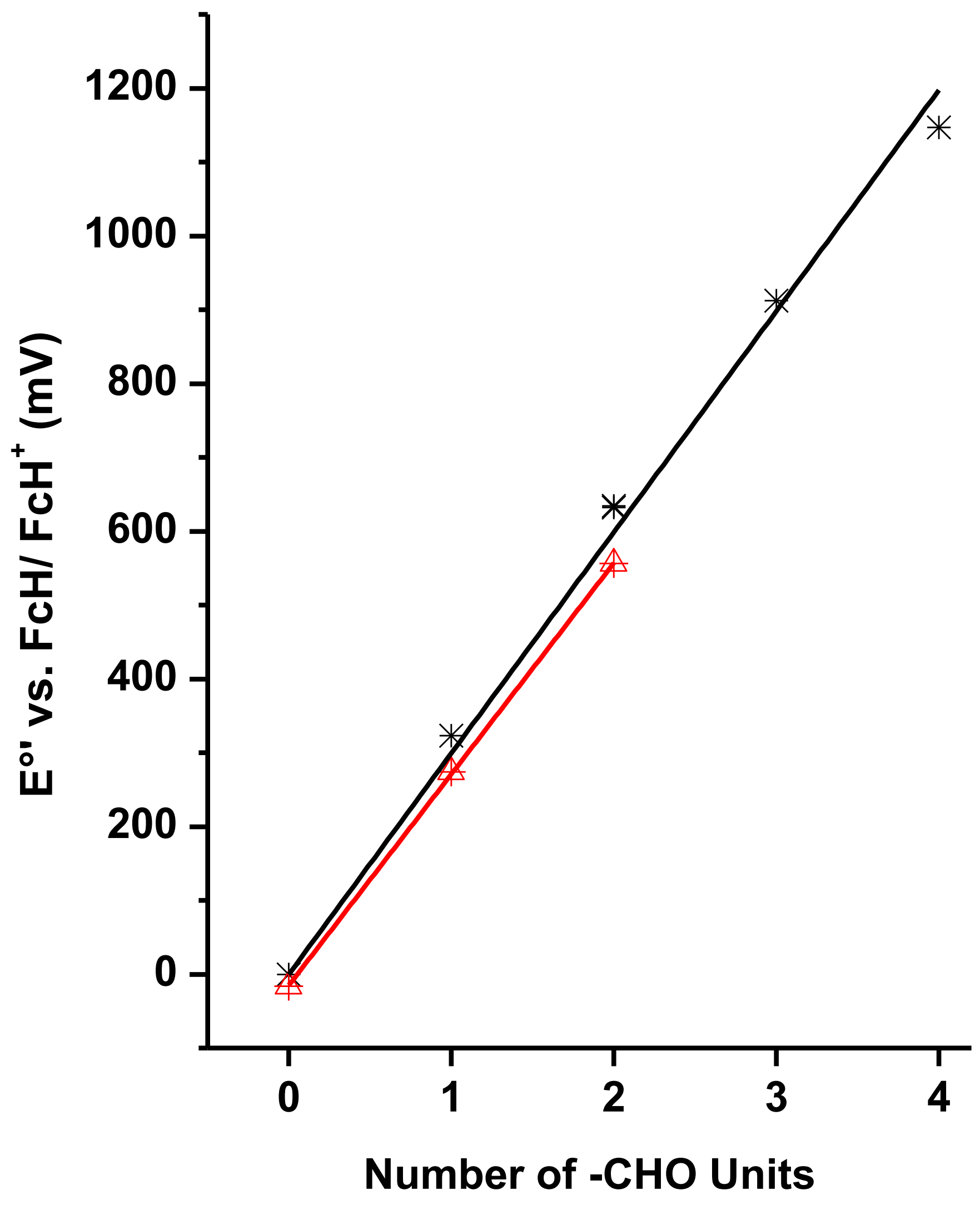


Figure 4. Redox potential of formyl-, 1,1′-diformyl-, 1,2-diformylferrocene, **3** and **6** (black line) and **1**, **2** and **4** (red line) in dependency of the number of CHO units.

Conclusion

Multi-functionalized ferrocene have been synthesized using a straightforward methodology, which included selective mono- or di-ortholithiation of 1,1′-di(1,3-dioxan-2-yl)ferrocene, subsequent quenching with dimethylformamide and deprotection of the acetal moiety afford tri- and tetra-formylferrocenes. The respective vinyl derivatives where synthesized via Wittig reaction. Electrochemical measurements showed that these electron poor ferrocenes become unstable in the cationic oxidation state. The irreversible behavior could be prevented by using weakly coordinating supporting electrolytes and reducing the measurement temperature to –40 °C. Furthermore, a linear correlation between the number of formyl functionalities and the redox potential was found.

References and Acknowledgement

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