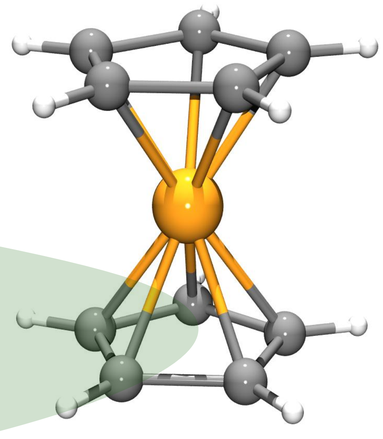
Tetraferrocenyl Five-Membered Heterocycles Electrochemistry in Multiredox Systems



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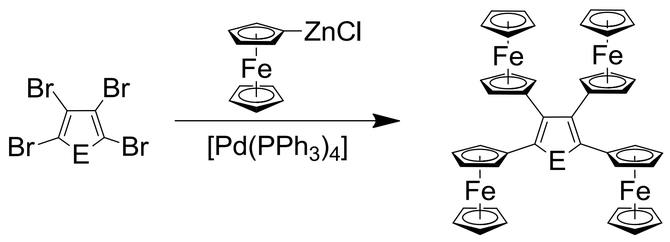
Introduction

Electronic communication in mixed-valent species has drawn increasing interest during recent years because they can act 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] We here present a series of multiferrocenyl functionalized heterocycles. Having similar geometries and therefor similar electrostatic properties, these molecules enable a direct correlation of the separation of the half wave potentials ($\Delta E_{1/2}$) and the intermetallic communication through the appropriate heterocyclic core. [2 – 4]

Synthetic Aspects

The 2,3,4,5-tetraferrocenyl-substituted heterocycles are accessible by Negishi ferrocenylation of the appropriate tetrabromo-substituted derivatives with FcZnCl (**2**) (Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4)), prepared by mono-lithiation of ferrocene according to Mueller-Westerhoff followed by treatment with dry zinkchloride, in presence of catalytic amounts of tetrakis(triphenylphosphino)palladium(0) (Scheme 1).



E = S (**1**), O (**2**), NMe(**3**), NPh (**4**)

Scheme 1*. Synthesis of the tetraferrocenyl heterocycles **1** – **4**.*

Dynamic NMR Studies

The identity of all molecules was proven by elemental analyses, ESI-MS, IR, UV and NMR experiments. To examine the rotation barrier of the ferrocenyl units in super crowded pyrrole **4** additional dynamic NMR studies (Figure 1) were performed.

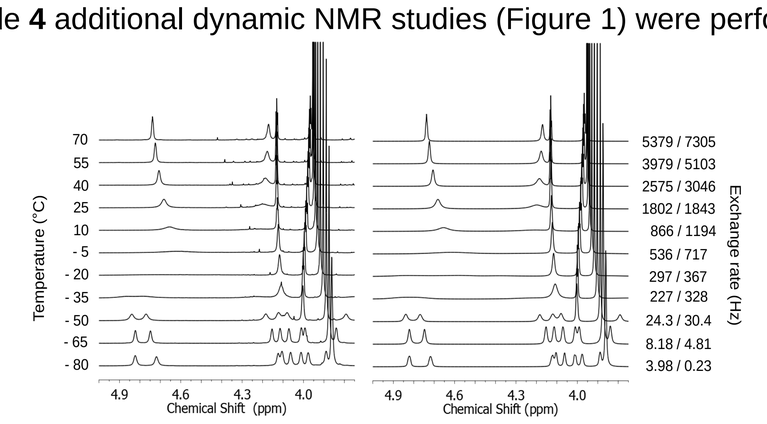


Figure 1. *Left: experimental ^{1}H NMR spectra of **4**, right: simulated ^{1}H NMR spectra of **4** with different exchange rates (Protons of ferrocenyls in 2,5 position / Protons of ferrocenyls in 3,4 position);* ferrocenyls in 2 and 5 position: $\Delta H^{\ddagger}$ = 26.8 (± 1.2) kJ·mol^{-1}, $\Delta S^{\ddagger}$ = -94.1 (± 4.5) J·mol^{-1}·K^{-1}, in 3 and 4 positions: $\Delta H^{\ddagger}$ = 27.9 (± 1.5) kJ·mol^{-1}, $\Delta S^{\ddagger}$ = -88.6 (± 5.6) J·mol^{-1}·K^{-1}.

Electrochemistry

The redox properties of heterocycles **1** – **4** were studied by cyclovoltammetry (Figure 2) and square wave voltammetry (Figure 3). As supporting electrolyte 0.1 mol·L^{-1} dichloromethane solutions of [N^{n}Bu$_4$][B(C_6F_5)$_4$] were used. It is possible to consecutively oxidize the ferrocenyls in all heterocycles *in situ* generating mono-, di-, tri- and tetra-cations. Each of the four ferrocenyl related redox processes show a reversible electrochemical behavior with 60 < ΔE_p < 72 mV. The $\Delta E_{1/2}$ values between the 1st and the 2nd redox event of phenylpyrrole **4** (331 mV) is the biggest in this series followed by methylpyrrole **3** (265 mV), furan **2** (227 mV) and thiophene **1** (219 mV).

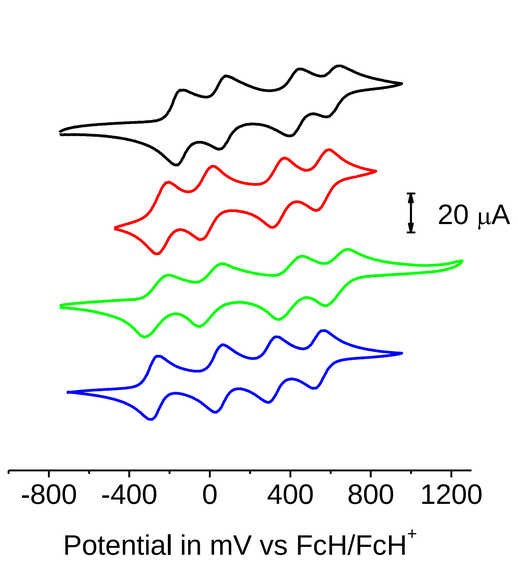
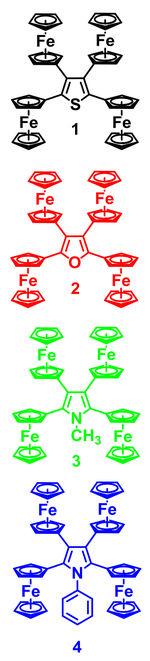


Figure 2. *Cyclovoltammograms of the molecules **1** – **4**.*



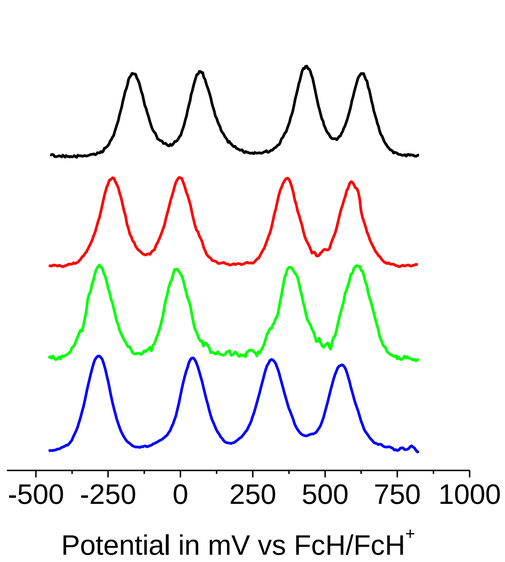


Figure 3. *Square wave voltammograms of the molecules **1** – **4**.*

The cyclovoltammetric data reveal that the intermetallic communication should be increased using electron rich heterocyclic core systems, as for example the here shown pyrroles (**3**, **4**), while electron poor furan (**2**) and thiophene (**1**) show far less separation of the redox events.

Spectro-Electrochemistry

The spectro-electrochemical studies were performed by stepwise increasing the potential from -500 to 1200 mV *vs* Ag/Ag$^+$ in an OTTLE cell (OTTLE = Optically Transparent Thin-Layer Electrode) containing dichloromethane solutions of **1** – **4** (1.0 mmol·L^{-1}) and [N^{n}Bu$_4$][B(C_6F_5)$_4$] (0.1 mol·L^{-1}) as electrolyte. During this procedure the neutral compounds **1** – **4** were stepwise oxidized and changes in their NIR spectroscopic properties could be monitored. IVCT absorptions in the monocationic oxidation state: 0 (**1**), 466 (**2**), 1045 (**3**), 4900 L·mol^{-1}·cm^{-1} (**4**).

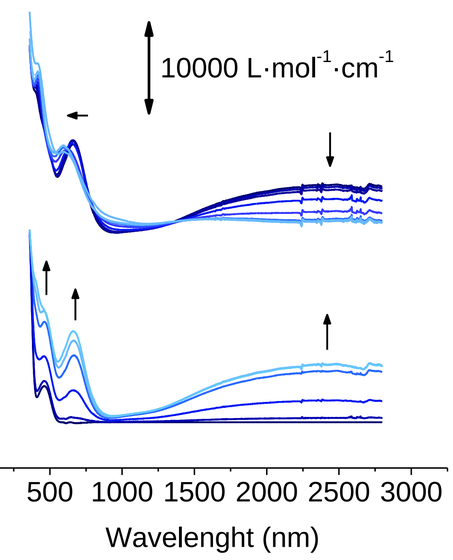


Figure 4. *NIR spectra of **4** at rising potentials (bottom, -500 to 200 mV; top: 250 to 525 mV vs Ag/AgCl).*

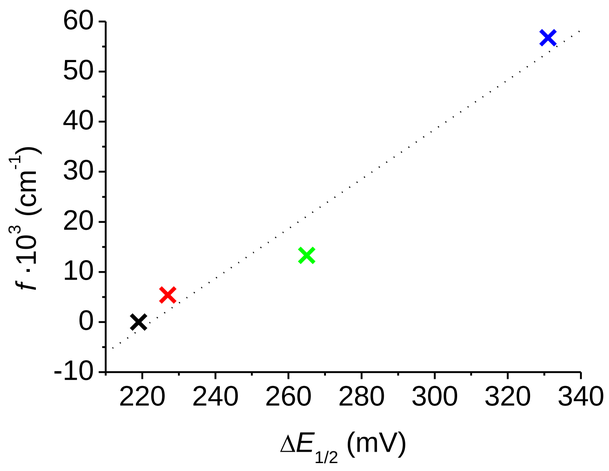


Figure 5. *Correlation of the oscillator strength f of the IVCT absorption and the $\Delta E_{1/2}$ values of **1** – **4**.*

For the first time in organometallic chemistry a linear relationship between the oscillator strength *f* of the IVCT absorption and $\Delta E_{1/2}$ was observed (Figure 5) which is consistent with the Hush theory assuming similar geometries and similar electrostatic properties. Therefore heterocycles **2** – **4** could be classified as class II systems according to Robin and Day, while molecule **1** can be assigned to class I, as the ferrocenyls do interact just electrostatically.

Conclusion

A series of 2,3,4,5-tetraferrocenyl heterocycles including thiophene, furan and pyrrole could be synthesized using the Negishi ferrocenylation methodology. Electro- and spectro-electrochemical studies such as cyclovoltammetry and square wave voltammetry as well as *in situ* NIR studies were performed to investigate the redox behavior and electron transfer properties of the heterocyclic compounds. These molecules show a linear relationship between the $\Delta E_{1/2}$ values and the oscillator strength *f* of the IVCT transitions as predicted by theoretical hypothesis for a series of molecules with similar geometries and hence, similar electrostatic properties. This relation could be described for the first time in organometallic chemistry.

References

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[2] A. Hildebrandt, T. Rüffer, E. Erasmus, J. C. Swarts, H. Lang *Organometallics* **2010**, *29*, 4900-4905.
[3] A. Hildebrandt, D. Schaarschmidt, H. Lang, *Organometallics*, Article ASAP **DOI:** 10.1021/om100914m.
[4] A. Hildebrandt, D. Schaarschmidt, L. van As, J. C. Swarts, H. Lang *Inorg. Chim. Acta* accepted.

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