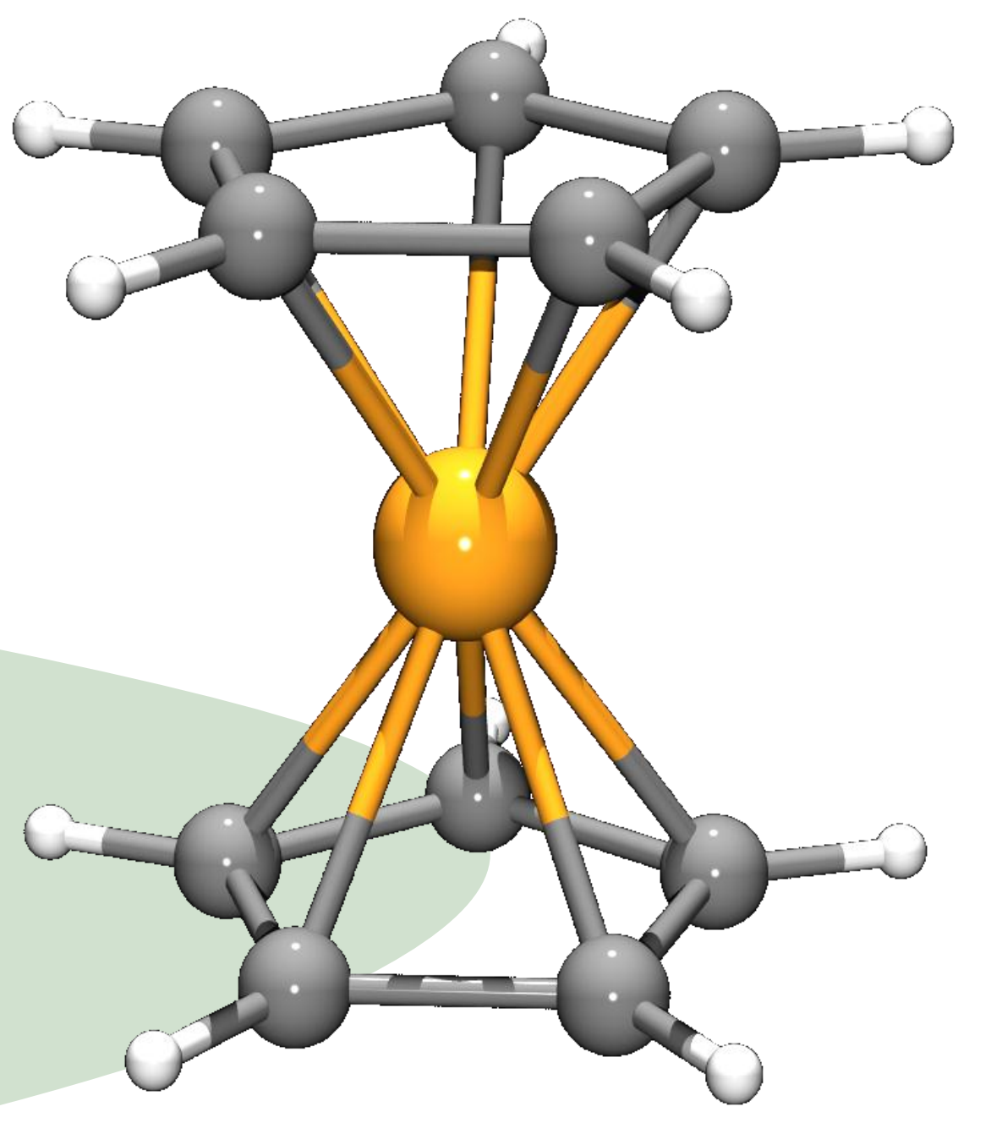
Electron Transfer Studies on Ferrocenyl substituted Thiophenes



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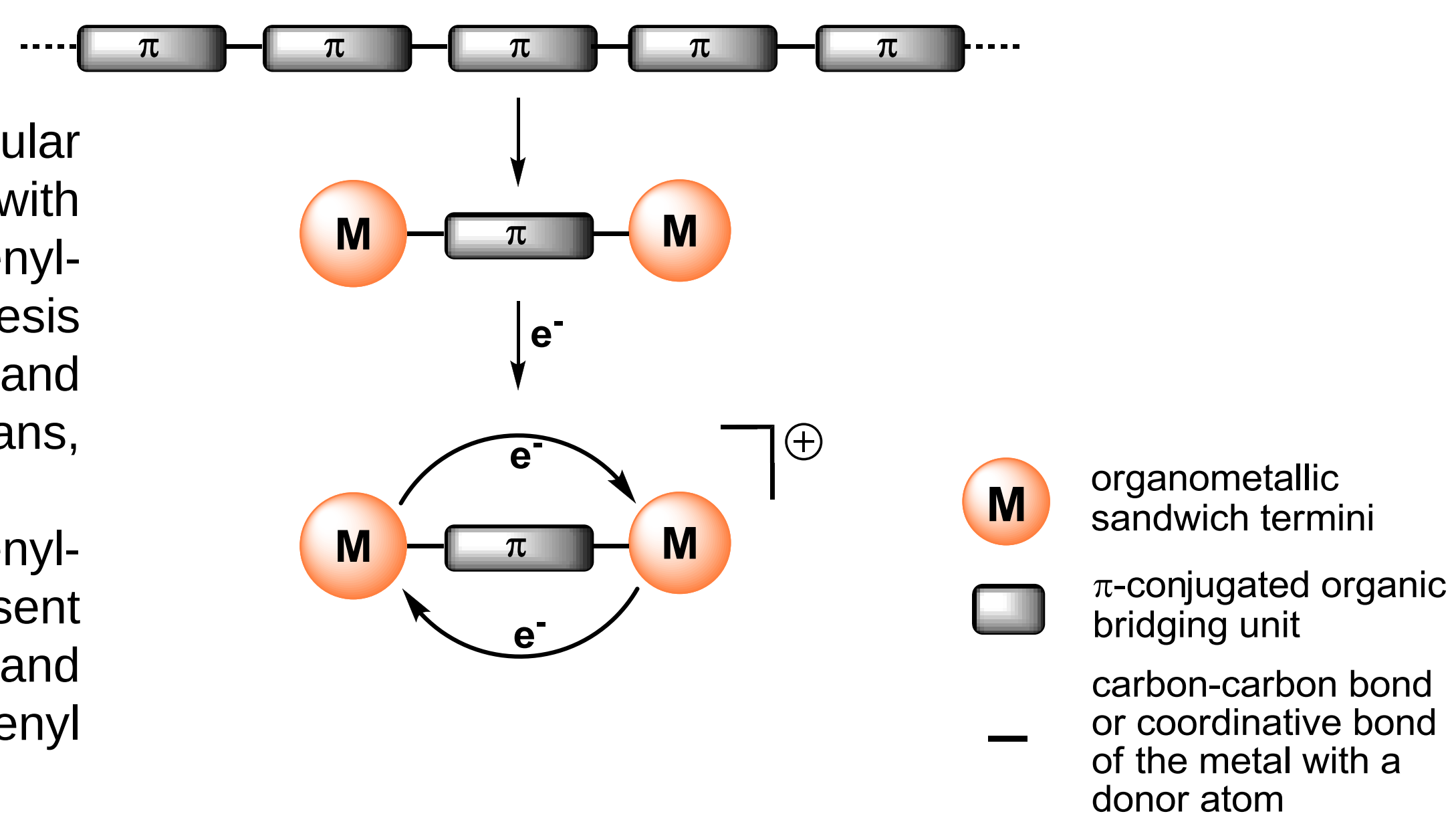
Introduction

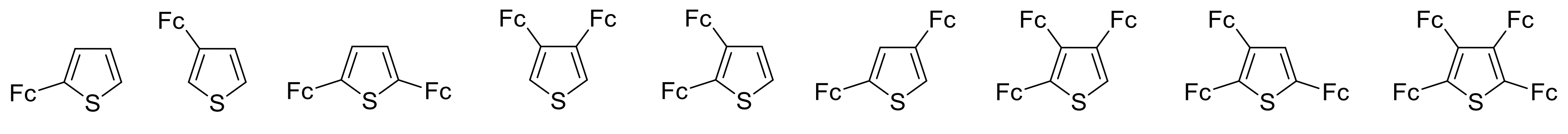
During recent years the development of compounds with redox-active metal centres has attracted considerable attention since they can be applied as new materials with novel chemical, physical and/or electronic properties in the field of material science.[1] Therefore, homo- and heterodinuclear complexes connected by *π*-conjugated organic units were designed as simple models for molecular wires[2] and novel electro-active materials.[3] Complexes with ferrocenyls as redox-active termini are extensively explored[4] focusing on the electrochemical behavior and on electron transfer processes.

Motivation

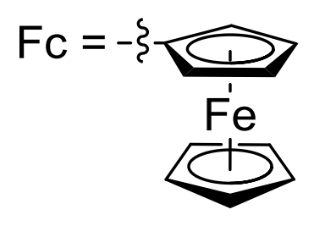
To investigate electron transfer in molecular wires, it is useful to study molecules with short bridging units between ferrocenyl-termini. Recently, we reported the synthesis and characterization of a series of 2,5-di- and 2,3,4,5-tetraferrocenyl substituted furans, thiophenes and pyrroles.[5]
In continuation of our work on ferrocenyl-functionalized heteroaromatics, we present here the design, the electrochemical and spectroelectrochemical behavior of ferrocenyl substituted thiophenes.



Ferrocenylthiophenes[6,7]

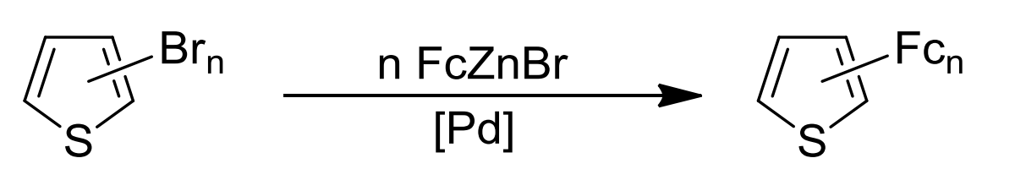


1 **2** **3** **4** **5** **6** **7** **8** **9**



The electrochemical and spectroelectrochemical properties of a series of mono-, di-, tri- and tetra-ferrocenyl thiophenes are reported.

Synthesis



n = 1, 2, 3, 4
[Pd] = $[Pd(CH_2CMe_2P^tBu_2)(\mu\text{-}Cl)]_2$

Scheme 1: Synthesis of Ferrocenyl Thiophenes.

The ferrocenylthiophenes **1** – **9** were synthesized applying a palladium-promoted Negishi *C,C* cross-coupling protocol, in which FcZnCl was treated with the corresponding bromothiophene, as catalysts $[Pd(CH_2CMe_2P^tBu_2)(\mu\text{-}Cl)]_2$ was used.
After appropriate work-up, molecules **1** – **9** could be isolated as either orange or red solid materials.

Electrochemistry

Compd.	$E_{1/2}/\Delta E_p/\Delta E_{1/2}$ [mV] (i_{pc}/i_{pa}) Wave (no.) (1)	(2)	(3)	(4)
1	16/60 (0.99)			
2	-9/67 (0.99)			
3	-53/60 (1.00)	195/62/248 (1.00)		
4	-49/71 (0.99)	195/70/244 (1.00)		
5	-51/71 (0.99)	232/73/283 (0.99)		
6	-21/68 (0.98)	148/69/169 (0.98)		
7	-118/63 (0.99)	148/61/266(0.99)	427/61/279 (1.00)	
8	-71/66 (1.00)	151/62/222 (0.99)	374/70/223 (1.00)	
9[6]	-161/62 (1.00)	58/64/219 (1.00)	418/64/360 (0.99)	604/60/186 (0.99)

Table 1: Cyclovoltammetric data (potentials *vs* FcH/FcH$^+$) of 1.0 mmol·L^{-1} solutions of **1** - **9** in dry dichloromethane containing 0.1 mol·L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C.

These ferrocenylthiophenes display either one (**1**, **2**), two (**3**, **4**, **5**, **6**), three (**7**, **8**) or four (**9**) well resolved electrochemically reversible one-electron transfer processes using $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte.

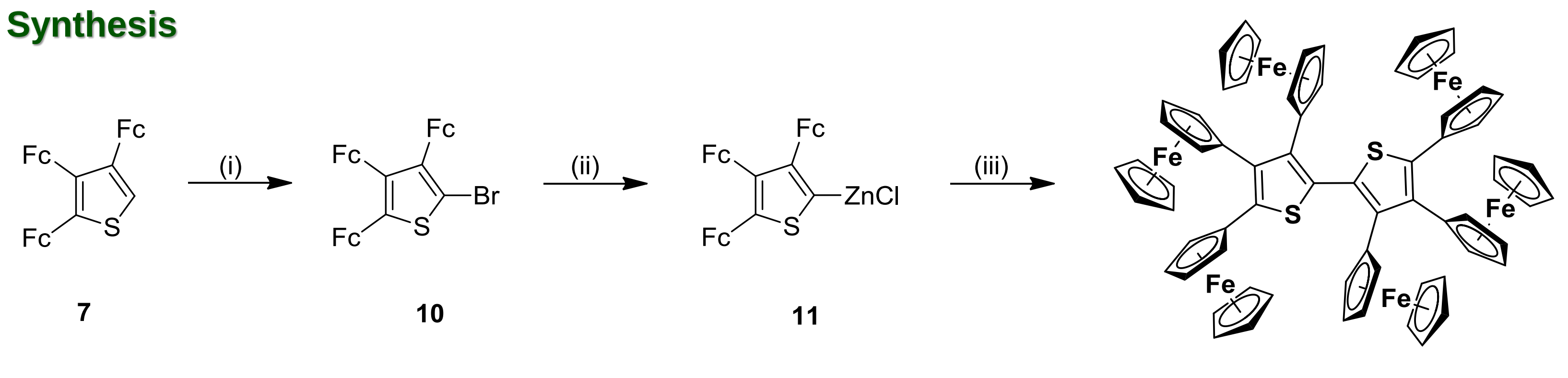
Compd.	ν_{max} [cm^{-1}] (ε_{max} [Lmol^{-1}cm^{-1}])	$\Delta\nu_{1/2}$ [cm^{-1}]	$\Delta\nu_{1/2(theo)}$ [cm^{-1}] $\{\Delta\nu_{1/2(theo)} = (2310\nu_{max})^{1/2}\}$
3$^+$	4994 (2129)	3843	3397
4$^+$	5405 (70)	7761	3534
5$^+$	5300 (401)	5492	3499
6$^+$	6098 (151)	5620	3753
7$^+$	6628 (184)	5736	3913
7^{2+}	7511 (244)	6733	4165
8$^+$	4861 (1583)	4628	3351
8^{2+}	5975 (639)	5895	3715

Table 2: NIR data, regarding IVCT absorptions, of in situ generated cationic intermediates from thiophenes **1** – **8** measured in an OTTLE cell, using dry dichloromethane containing 0.1 mol·L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C.

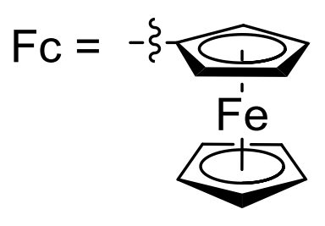
The spectroelectrochemical studies suggest weak metal-metal interactions in the intervalent species (Table 2), while class II systems typically show bandwidths 30-40% in excess of the Hush prediction $\Delta\nu_{1/2(theo)}$ (due to various contributory factors overlooked in Hush's treatment). Thus, Table 2 compares experimental and predicted values of $\Delta\nu_{1/2}$; the comparison is clearly consistent with the identification of the low-energy absorption of this class of compounds as class II mixed-valence IVCT bands.[8] However, during a stepwise oxidation of **9** no notable transitions which could be attributed to IVCT absorptions were observed in the NIR region.[6]

3,3',4,4',5,5'-Hexaferrocenyl-2,2'-bithiophene[9]

Synthesis



7 **10** **11** **12**



Scheme 2: Consecutive synthesis of 3,3',4,4',5,5'-hexaferrocenyl-2,2'-bithiophene (**12**). Conditions: (i) Tetrahydrofuran; *1st*: ^{n}BuLi, -25 °C, 35 min; *2nd*: 1,1,2,2-tetrabromoethane, 25 °C, 1 h. (ii) Tetrahydrofuran; *1st*: ^{n}BuLi, -50 °C, 45 min; *2nd*: $[ZnCl_2{\cdot}2thf]$, 0 °C, 1 h. (iii) *1st*: **10**, *2nd*: [Pd], 55 °C, 48 h ([Pd] = $[Pd(CH_2CMe_2P^tBu_2)(\mu\text{-}Cl)]_2$).

3,3',4,4',5,5'-Hexaferrocenyl-2,2'-bithiophene (**12**) has been prepared using a straightforward synthesis protocol which follows the palladium-promoted Negishi *C,C* cross-coupling of bromothiophene **10** with the organozinc compound **11**. After appropriate work-up, the ferrocenyl-substituted compounds **10** and **12** could be obtained as orange solids. They have been identified by NMR (^{1}H, ^{13}C{^{1}H}) and IR spectroscopy as well as elemental analysis. Additionally, high resolution ESI-TOF mass spectrometric and single crystal X-ray diffraction studies have been determined.

Dynamic 1H-NMR spectroscopy

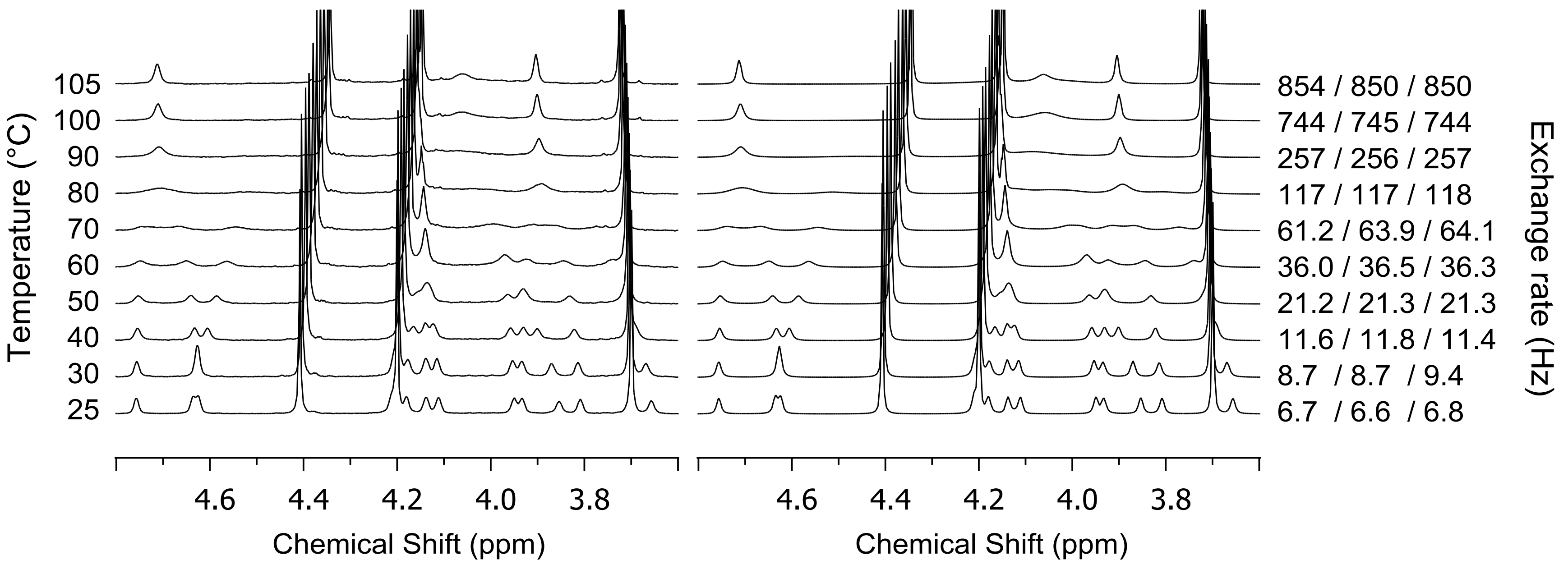


Figure 1: Left: ^{1}H NMR spectra of **12** in the range of 3.6 and 4.8 ppm at various temperatures (toluene-d$_8$).
Right: Simulated ^{1}H NMR spectra of **12** with different exchange rates.

The activation parameters of the inner bithiophene *C,C* bond rotation could be quantified from the exchange rates using graphical methods according to Eyring. Values for the activation enthalpy $\Delta H^‡$ = 54.3 (±4.0) kJ mol^{-1} and activation entropy $\Delta S^‡$ = -50.3 (±11.8) J K^{-1} mol^{-1} could be determined for the rotation barrier.

Electrochemistry

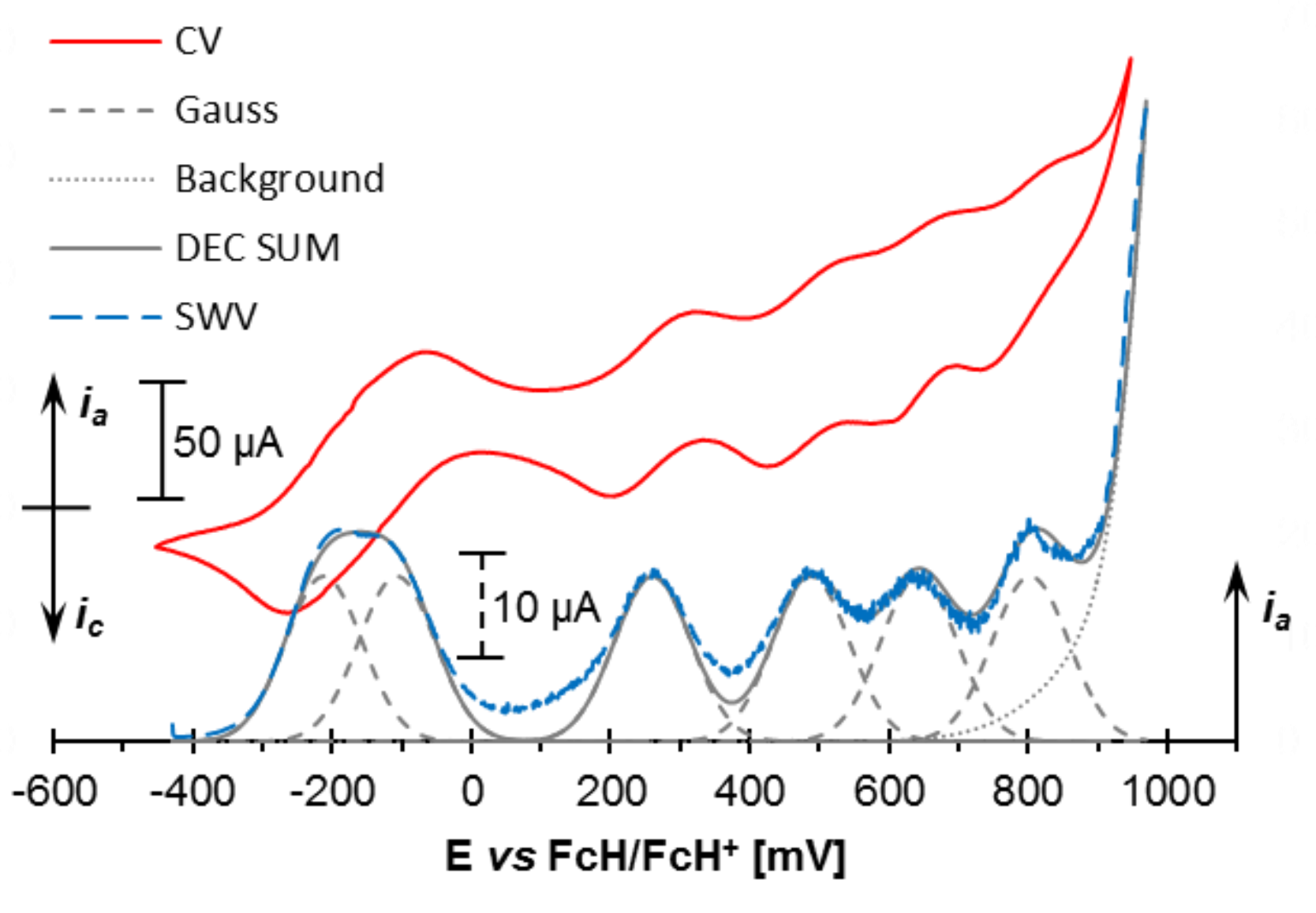


Figure 2: CV (scan rate: 100 mV, left ordinate) and SWV (1 Hz, right ordinate) of **12** in anisole solution (1.0 mmol·L^{-1}) at 100 °C, supporting electrolyte $[N^nBu_4][B(C_6F_5)_4]$ (0.1 mol·L^{-1}).

The Cyclovoltammogram (CV) of **12** (Figure 2) shows five waves at $E_{1/2}$ = -165, 261, 491, 651, and 800 mV as well as ΔE_p values between 71 and 78 mV according to one electron processes. However, the *1st* redox event shows a peak separation ΔE_p of 156 mV. This indicates that this wave corresponds to two redox events close together. Deconvolution of the square wave voltammogram (SWV) confirms this observation, whereas the superposition (DEC SUM) of all processes consists of six one-electron redox events (Gauss) and the increasing background current (Background) at the anodic end of the electrochemical window. Spectroelectrochemistry of **12** confirms that upon stepwise oxidation of the ferrocenyl termini and electrochemically generated ferrocenium units mostly communicate electrostatically with each other, since no notable transitions which could be attributed to IVCT absorptions were observed in the NIR region.

Solid state structure

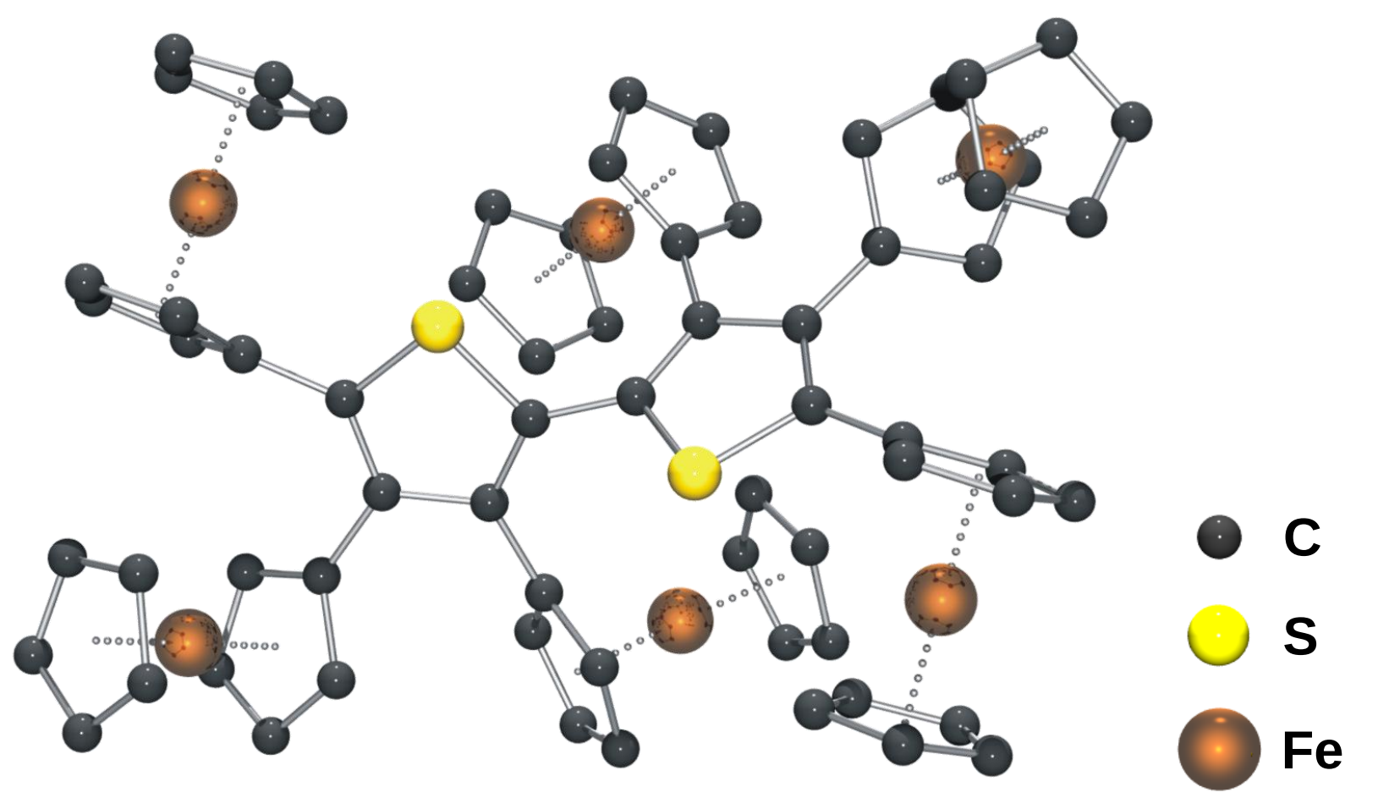


Figure 3: molecular structure of **12·1.5 C$_7$H$_8$**. All hydrogen atoms and 1.5 molecules of toluene have been omitted for clarity.

Bithiophene **12** crystallizes in the triclinic space group *P*-1 as orange plates. The X-ray structure analysis shows that the bithiophene core unit is not coplanar, since a torsion angle of 61.4(1)° was observed between the thiophene mean planes.

Conclusion

The electrochemical and spectroelectrochemical studies from a series of mono-, di-, tri- and tetra-ferrocenyl thiophenes suggest weak metal-metal interactions in the corresponding intermediates of the di- and triferrocenyl thiophenes. Furthermore, the atropisomeric 3,3',4,4',5,5'-hexaferrocenyl-2,2'-bithiophene is available in a straightforward palladium-promoted Negishi *C,C* coupling of 2-bromo-3,4,5-triferrocenylthiophene and 2,3,4-triferrocenyl-thiophene zinc chloride. The cyclic and square wave voltammograms highlight the electrochemical behavior of the organometallic compound. Additionally, UV-Vis/NIR measurements revealed that the electrochemically generated ferrocenium units mostly communicate electrostatically with each other, since no IVCT absorptions were found in the NIR region.

References and Acknowledgement

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