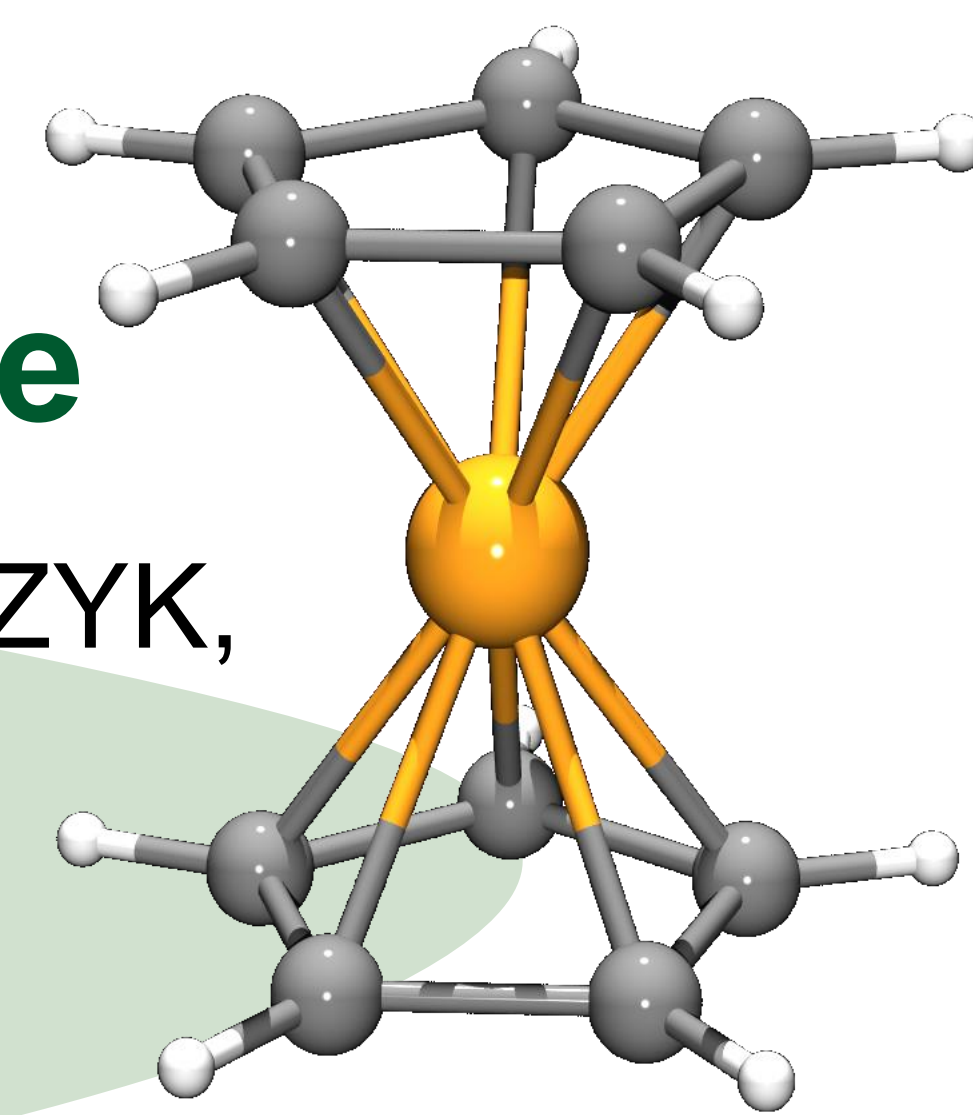




A new Ferrocenyl-functionalized Cyclic System – 1,3,5-Triethynylferrocenyl-2,4,6-triferrocenyl-benzene

Ulrike PFAFF, Alexander HILDEBRANDT, Marcus KORB, Grzegorz FILIPCZYK,
Heinrich LANG*

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry,
Inorganic Chemistry, 09107 Chemnitz, Germany.
ulrike.pfaff@chemie.tu-chemnitz.de



Introduction and Motivation

Multiferrocenyl-substituted aromatics and heteroaromatics are fascinating molecules not only for chemists. Besides the study of uncommon molecular structures, sterically crowded compounds are attractive for the investigation of their electronic properties. Some examples of this family are given by Vollhardt's hexaferrocenyl benzene^[1], Fehlner's tetraferrocenyl cyclobutadienyl cyclopentadienyl cobalt^[2] and the hexa-

ferrocenylethynyl benzene of Astruc^[3]. Multiferrocenyl-substituted heterocycles is one of the topics of our research group^[4]. The synthesis of a perferrocenylated benzene with alternating ferrocenyl and ferrocenylethynyl functionalities allowed us to enrich this family of compounds.

Synthesis and Characterization

Scheme 1. Synthesis of the title compound using Sonogashira and Negishi C,C cross coupling reactions.

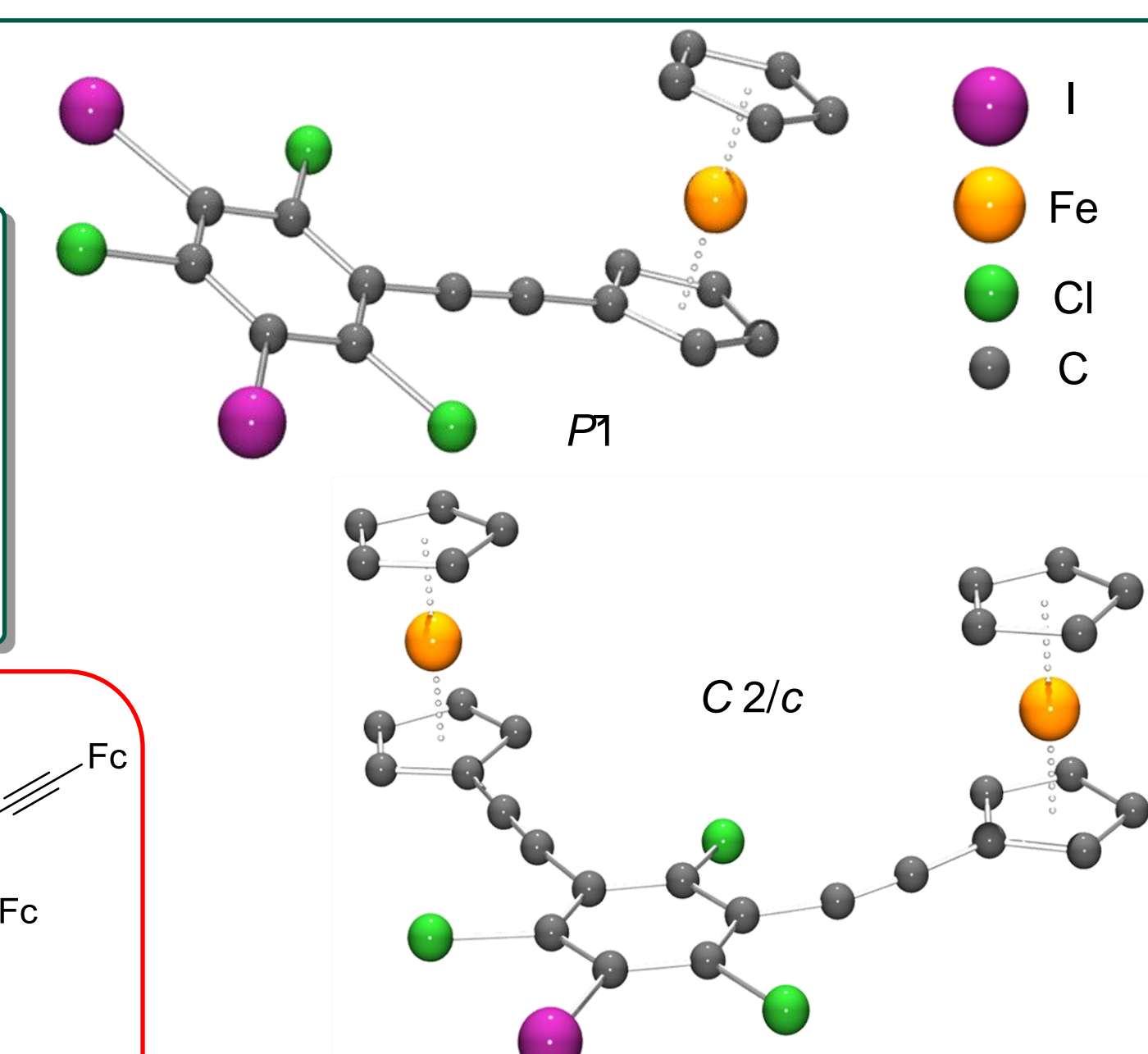
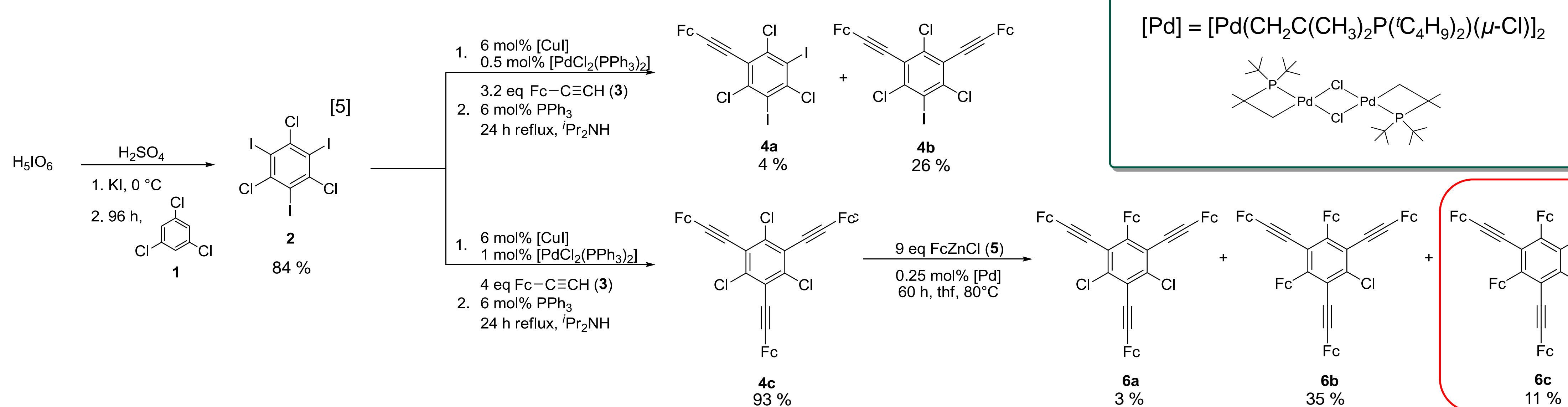


Fig. 1. Solid state structures of **4a** (top) and **4b** (below).

For the synthesis of **6c**, molecule **2**, which behaves selectively to Sonogashira and Negishi C,C cross-coupling reactions, was used. While reaction conditions with a slight excess of ethynylferrocene (**3**) afforded only the mono- and bis(ferrocenylethynyl)-substituted benzenes (**4a** and **4b**), the increase of the amount of **3** and of the catalyst [PdCl₂(PPh₃)₂] led to a nearly quantitative yield of **4c**. The introduction of the ferrocenyl units using an excess of FcZnCl (**5**) in the Negishi C,C cross-coupling reaction resulted in the formation of **6a-c** in the ratio of 1 : 11.2 : 3.6, whereby different stoichiometries of **5** and the catalyst had no significant influence. Compounds **4a-c** and **6a-c** have been characterized by NMR (¹H, ¹³C{¹H}) and IR spectroscopy as well as elemental analysis and high resolution ESI-TOF mass spectrometry. Additionally, single crystal X-ray diffraction studies have been determined (**4a**, **4b**) (Figure 1).

Electrochemistry and Spectroelectrochemistry

Table 1. Cyclic voltammetry data (potentials vs FcH/FcH⁺), scan rate 100 mV·s⁻¹ at a glassy-carbon electrode of 1.0 mmol·L⁻¹ solutions of the analytes in dry dichloromethane containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte at 25 °C.

| Compd | E ₁ ^o (mV) ^[a] | E ₂ ^o (mV) ^[a] | E ₃ ^o (mV) ^[a] | E ₄ ^o (mV) ^[a] | E ₅ ^o (mV) ^[a] | E ₆ ^o (mV) ^[a] | ΔE ^o (mV) ^[c] |
|-----------------------|---|---|---|---|---|---|-------------------------------------|
| | (ΔE _p (mV)) ^[b] | (ΔE _p (mV)) ^[b] | (ΔE _p (mV)) ^[b] | (ΔE _p (mV)) ^[b] | (ΔE _p (mV)) ^[b] | (ΔE _p (mV)) ^[b] | |
| 4a | 190 (71) | - | - | - | - | - | - |
| 4b | 195 (59) | - | - | - | - | - | - |
| 4c | 390 (58) | - | - | - | - | - | - |
| 6a | 40 (74) | 225 (108) | 360 (84) | - | - | - | 185/135 |
| 6b^d | -50 | 90 | 250 | 335 | 485 | - | 140/160/85/150 |
| 6c | -80 (75) | 70 (68) | 220 (69) | 420 (65) | 530 (63) | 660 (147) | 150/150/200/110/130 |

^aE^o = formal potential. ^bΔE_p = difference between the oxidation and the reduction potential. ^cΔE^o = potential difference between the two ferrocenyl-related redox processes. ^dValues determined with Square Wave Voltammetry

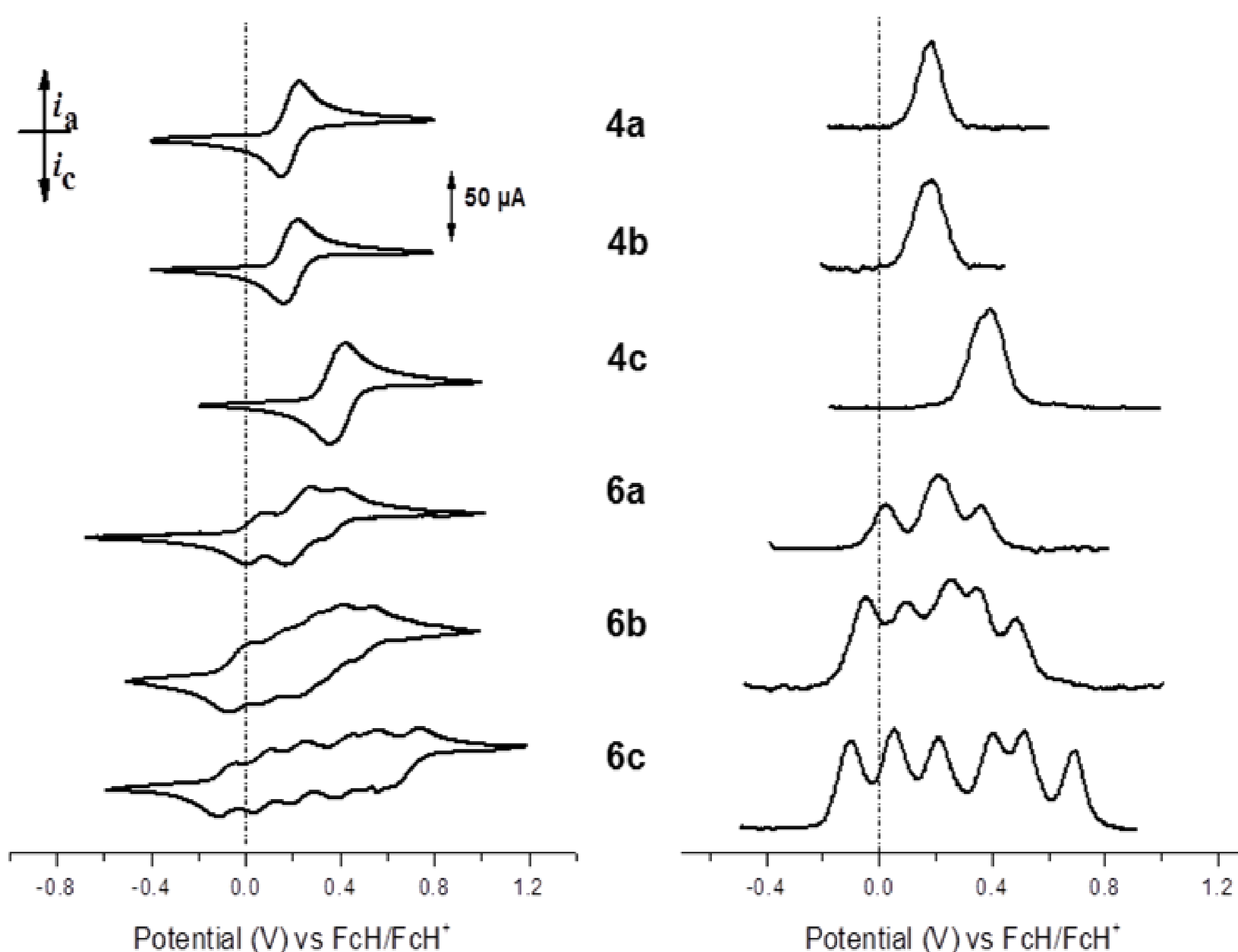


Figure 2. Cyclic (left) and square wave (right) voltammograms of **4a-c** and **6a-c** at 25 °C.

In Figure 2 the cyclic (CV) and square wave voltammograms (SWV) of **4a-c** show one reversible redox event. With an increasing number of ferrocenylethynyl units at benzene, the E₁^o values are shifted to anodic potentials indicating that the metal centers are more difficult to oxidize. Owing to the introduction of ferrocenyl groups (**6a-c**), the number of reversible redox events increases. One reason for the observable redox splitting is the increased contribution of the electrostatic factor (ΔE_e), due to larger steric demand (Equation 1).

$$\Delta E^o = \Delta E_e + \Delta E_s + 36 \text{ mV} + \Delta E_r \quad (1)$$

Noteworthy is the high ΔE_p value (108 mV, **6a**) of the second redox wave, suggesting that two individual reversible one-electron processes take place in a close potential range. To gain a deeper insight into the electronic properties of **6a-c** *in situ* spectroelectrochemical UV-Vis/NIR measurements have been carried out.

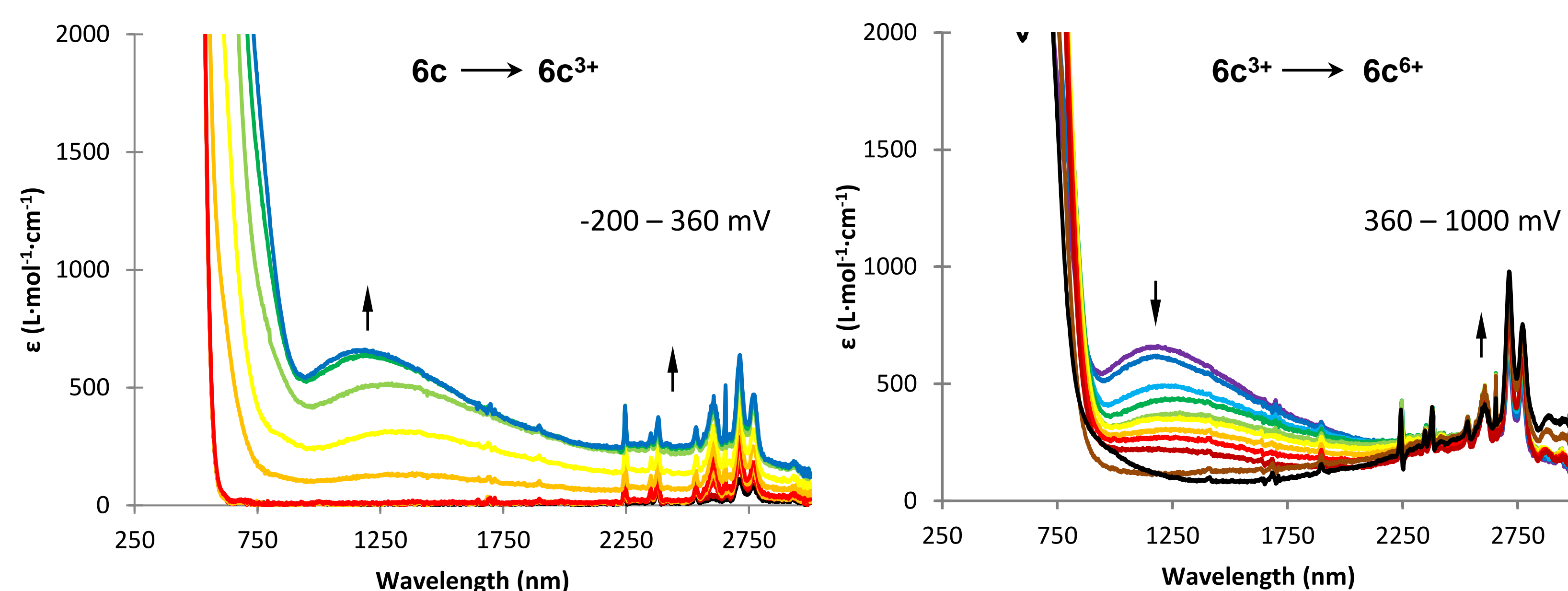


Figure 3. UV-Vis/NIR spectra of **6c** at rising potentials (100, 50, 15 mV steps) vs. Ag/AgCl in an OTTE cell. Measurement conditions: 25 °C, dichloromethane, 0.02 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)₄]. Arrows indicate increasing or decreasing absorptions.

For **6a-b** no absorptions in the NIR region could be observed upon subsequent oxidation. Merely, absorptions in the UV-Vis region (250 – 750 nm) including the π-π* transition of the benzene as well as the d-d transitions of the Fc substituents were detected. Compound **6c** shows a weak and broad excitation at 1170 nm, while oxidized. An assignment, which of the five possible mixed-valent species is recorded, is quite difficult to prove. We suggest that the mixed-valent species between **6c**³⁺ and **6c**⁴⁺ is observed, due to the applied potential.

Conclusion

A series of (multi)ferrocenyl-substituted benzenes have been prepared using the Sonogashira and Negishi C,C cross-coupling reaction protocol of halogenated aromatics with ethynylferrocene and ferrocenyl zinc chloride, respectively. The redox properties were studied by cyclic and square wave voltammetry. Separate redox processes could only be detected for **6a-c**, due to the increasing electrostatic contribution. Additional, *in situ* UV-Vis/NIR studies revealed IVCT transitions in the mixed-valent oxidation states classifying **6c** as weakly coupled class II system according to the classification of Robin and Day.^[6]

References

- [1] Y. Yu, A. D. Bond, P. W. Leonard, U. J. Lorenz, T. V. Timofeeva, K. P. C. Vollhardt, G. D. Whitener, A. A. Yakovenko, *Chem. Commun.* **2006**, 2572-2574.
- [2] J. Jiao, G. J. Long, F. Grandjean, A. M. Beatty, T. P. Fehlner, *J. Am. Chem. Soc.* **2005**, 127, 17819-17831.
- [3] a) A. K. Diallo, J.-C. Daran, F. Varret, J. Ruiz, D. Astruc, *Angew. Chem. Int. Ed.* **2009**, 48, 3141-3145; b) A. K. Diallo, C. Absalon, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2011**, 133, 629-641.
- [4] a) A. Hildebrandt, H. Lang *Organometallics* **2013**, 32, 5640-5653; b) J. M. Speck, D. Schaarschmidt, H. Lang, *Organometallics* **2012**, 31, 1975-1982; c) A. Hildebrandt, U. Pfaff, H. Lang *Rev. Inorg. Chem.* **2011**, 31, 111-141.
- [5] K. Kobayashi, N. Kobayashi, *J. Org. Chem.* **2004**, 69, 2487-97.
- [6] M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, 10, 247-422.