

Synthesis, Molecular Solid-State Structures and Electrochemical Behavior of Monoarylferrocenes

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Introduction

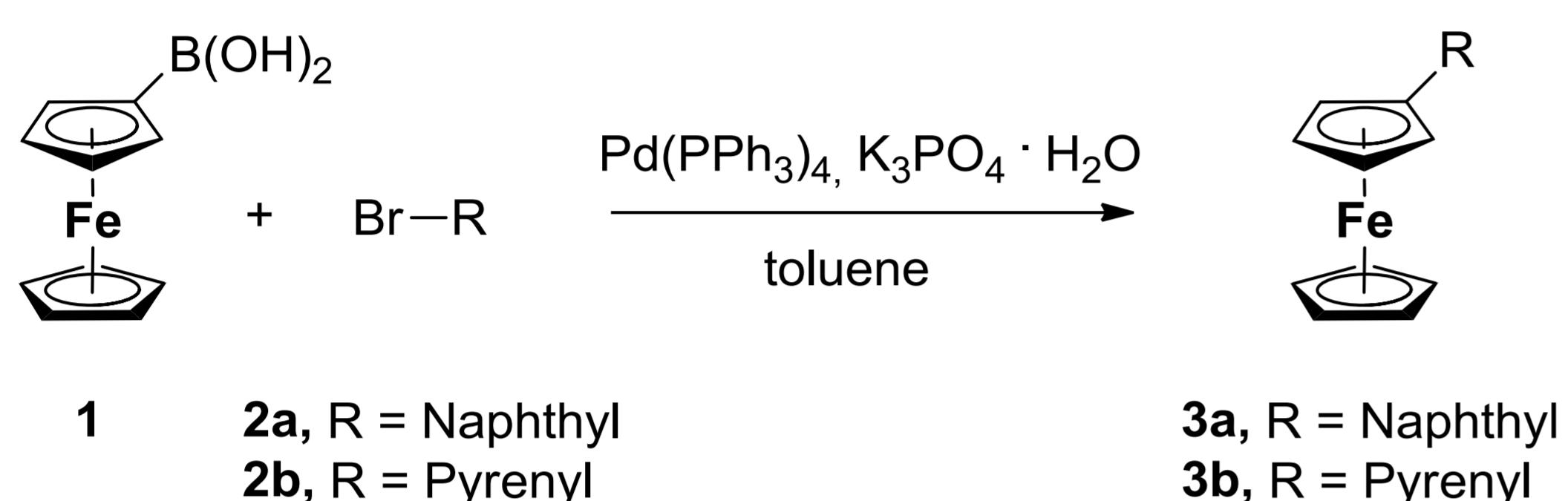
Ferrocene derivatives are widely studied due to their electron-donating ability, electrochemical reversibility^[1] and, for example, the non-linear optical behavior.^[2] The combination of ferrocene with aromatics, such as naphthalene and pyrene, resulted in interesting optical characteristics of these monoaromatic species.^[3,4] Hence, we are interested in the charge transfer properties of such monoaryl-functionalized ferrocenes.

β -Naphthylferrocene **3a** and 1-ferrocenylpyrene **3b** are accessible by the reaction of ferrocenyl boronic acid with the respective aryl-bromides by the Pd-catalyzed Suzuki C,C cross-coupling reaction.

We herein present the synthesis, as well as the chemical and physical properties, including the electrochemical and spectroelectrochemical (*in situ* UV-vis/NIR) behavior of **3a**.

Synthesis

Ferrocenes **3a** and **3b** were synthesized by the reaction of ferrocenyl boronic acid with the respective aryl-bromides by the Pd-catalyzed Suzuki C,C cross-coupling reaction (Scheme 1).



Scheme 1. Synthesis of monoarylferrocenes **3a** and **3b** using the Suzuki C,C cross coupling protocol.

The structures of **3a** and **3b** in the solid state were determined by single crystal X-ray diffraction analysis. Suitable crystals were obtained by slow evaporation from a concentrated dichloromethane solution at ambient conditions. The ball and stick diagrams of both compounds are presented in Figure 1. Compound **3a** crystallizes in orthorhombic space group, while **3b** crystallizes in monoclinic space group.

In **3a** the naphthyl unit is almost coplanar to the C_5H_4 building block ($2.1 (4)^\circ$). Sandwich compound **3b** has a torsion angle for the substituted cyclopentadienyl unit to the pyrenyl unit of $-38.9 (3)^\circ$. The pyrenyl moiety is significantly twisted against the C_5H_4 building block of ferrocene.

X-ray Discussion

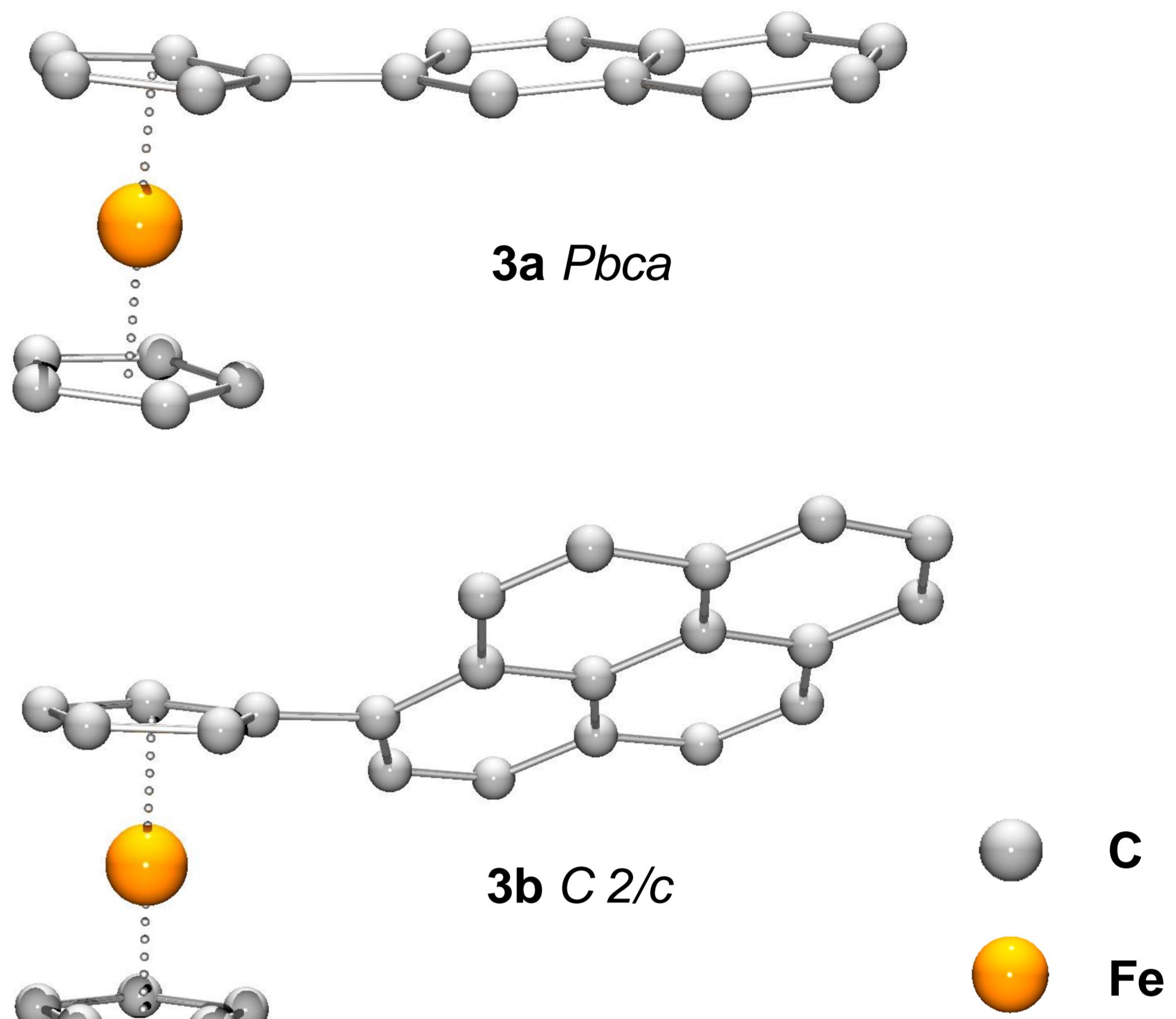


Figure 1. Solid state structure of **3a** (top) and **3b** (below).

(Spectro)Electrochemistry

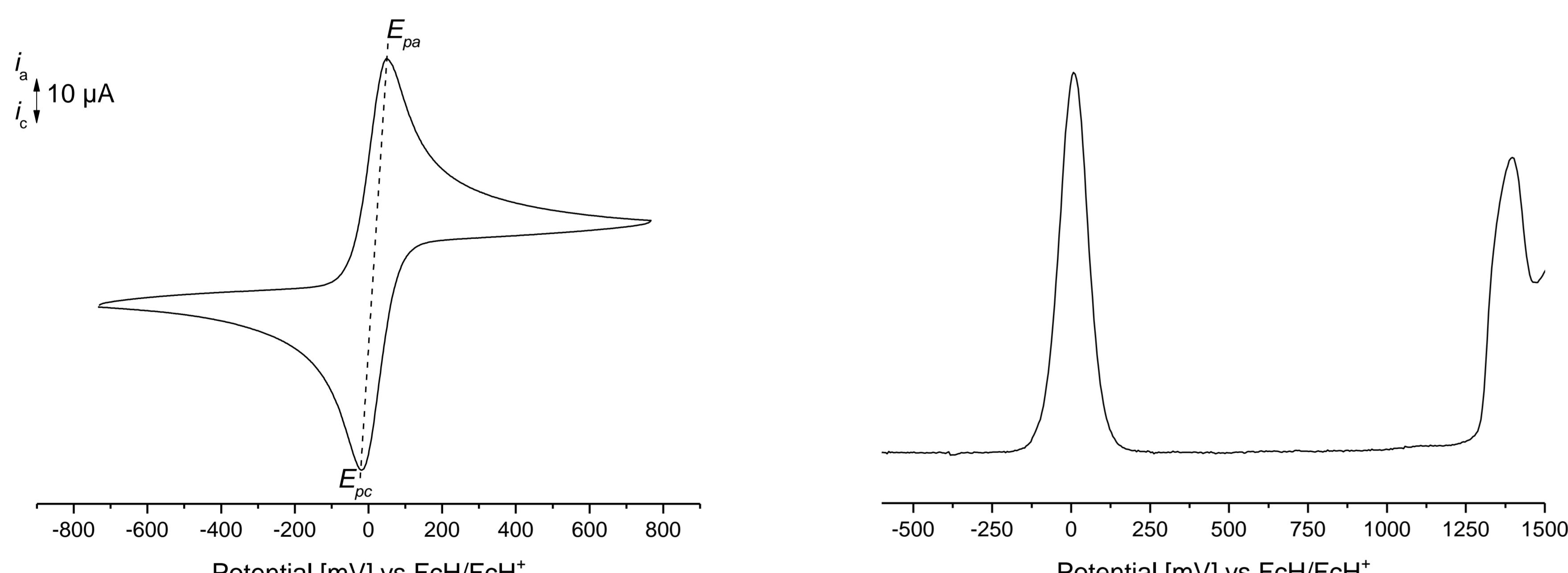


Figure 2. Cyclic voltammogram of **3a**; scan rate $100 \text{ mV} \cdot \text{s}^{-1}$ at glassy carbon electrode, $1.0 \text{ mmol} \cdot \text{L}^{-1}$ solution in anhydrous dichloromethane; $0.1 \text{ mmol} \cdot \text{L}^{-1} [N^{\text{Bu}}_4][B(C_6F_5)_4]$ as supporting electrolyte at 25°C .

Table 1. Cyclic voltammetry data (potentials vs FcH/FcH^+) of **3a** and **3b** at 25°C .

Compound	$E_1^{\circ\circ} (\text{mV})^{[a]}$ ($\Delta E_p (\text{mV})^{[b]}$)	$E_2^{\circ\circ} (\text{mV})^{[a]}$ ($\Delta E_p (\text{mV})^{[b]}$)
3a	15 (70)	1398 ^[c]
3b	35 (73)	1084 (84)

^a $E^{\circ\circ}$ = formal potential. ^b ΔE_p = Difference between the oxidation and the reduction potential. ^cValues determined with Square wave voltammetry.

Figure 3. Square wave voltammogram of **3a**; $1.0 \text{ mmol} \cdot \text{L}^{-1}$ solution in anhydrous dichloromethane; $0.1 \text{ mmol} \cdot \text{L}^{-1} [N^{\text{Bu}}_4][B(C_6F_5)_4]$ as supporting electrolyte at 25°C .

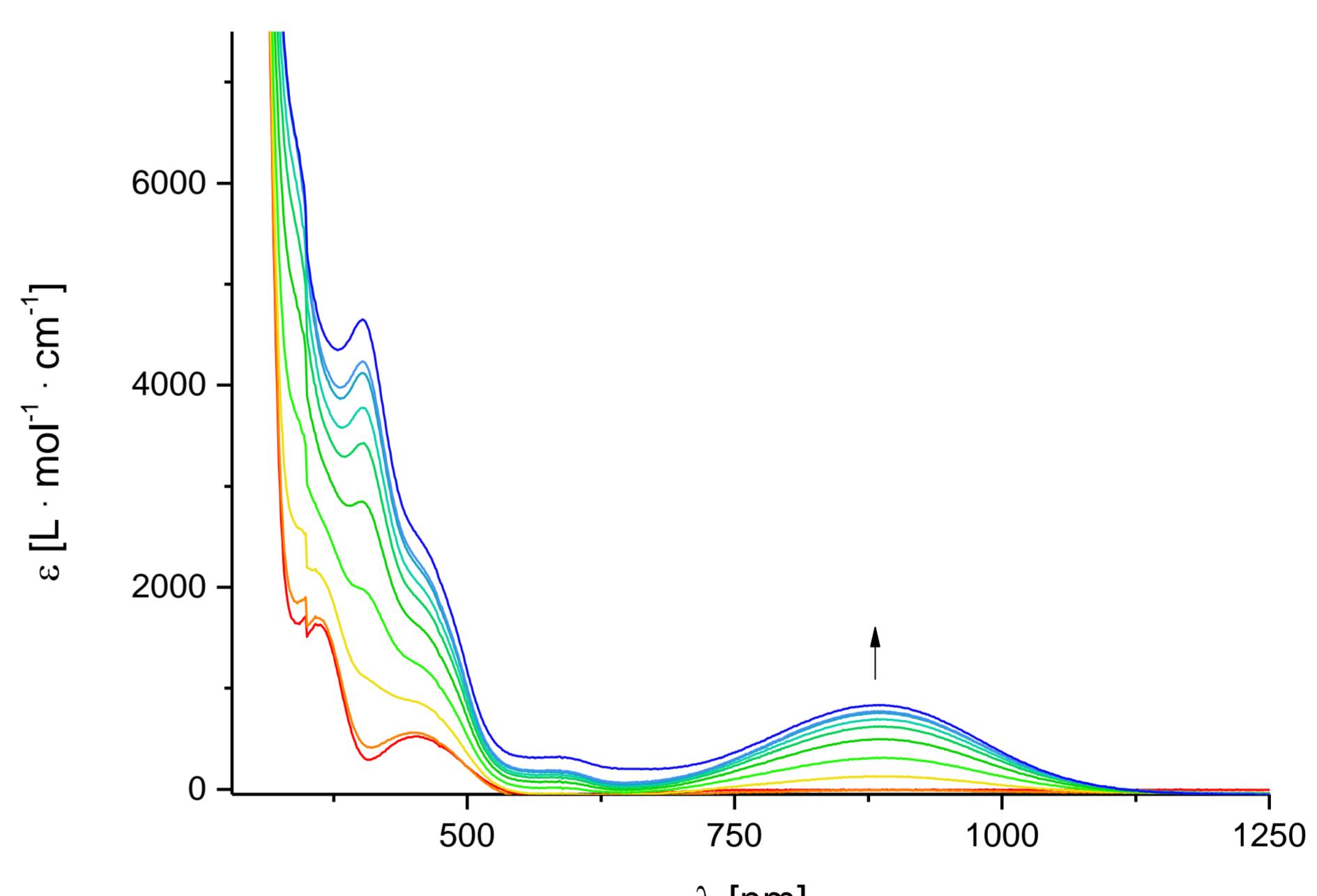


Figure 4. UV-Vis/NIR spectra of **3a** at rising potentials (100, 50, 25 mV steps) vs Ag/AgCl in an OTTLE cell; measurement conditions: 25°C , dichloromethane, $0.02 \text{ mmol} \cdot \text{L}^{-1} [N^{\text{Bu}}_4][B(C_6F_5)_4]$, arrows indicate increasing of absorptions.

The cyclic voltammogram (CV) (Figure 2) of **3a** shows one reversible redox event. With increasing size of the aryl group at ferrocene, the $E_1^{\circ\circ}$ value is shifted to anodic potentials indicating that the metal centre is more difficult to oxidize. The 2nd redox event of the naphthyl unit of **3a** is observed at 1398 mV by square wave voltammetry (Figure 3). The aromatic unit of **3b** with a redox potential at 1084 mV is more easily oxidized than the naphthyl building block of **3a** (Table 1). To gain a deeper insight into the electronic properties of **3a** *in situ* spectroelectrochemical UV-vis/NIR measurement has been carried out. Compound **3a** shows a weak and broad excitation at 880 nm, while oxidized. This absorption represents a charge transfer band, which is assigned to the LMCT transition from naphthyl to ferrocenium.^[3,5]

Conclusion and Outlook

Sandwich compounds **3a** and **3b** have been prepared by the Pd-catalyzed Suzuki C,C cross coupling reaction protocol of ferrocenyl boronic acid with the respective aryl-bromide. The structures of both sandwich compounds in the solid state were determined by single crystal X-ray diffraction studies. The redox properties were studied by cyclic and square wave voltammetry. With increasing size of the aryl group at the ferrocene, the $E_1^{\circ\circ}$ value is shifted to anodic potentials indicating that the metal centre is more difficult to oxidize. Additional, *in situ* UV-vis/NIR studies revealed a LMCT from naphthyl unit to ferrocenium.

References and Acknowledgement

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