

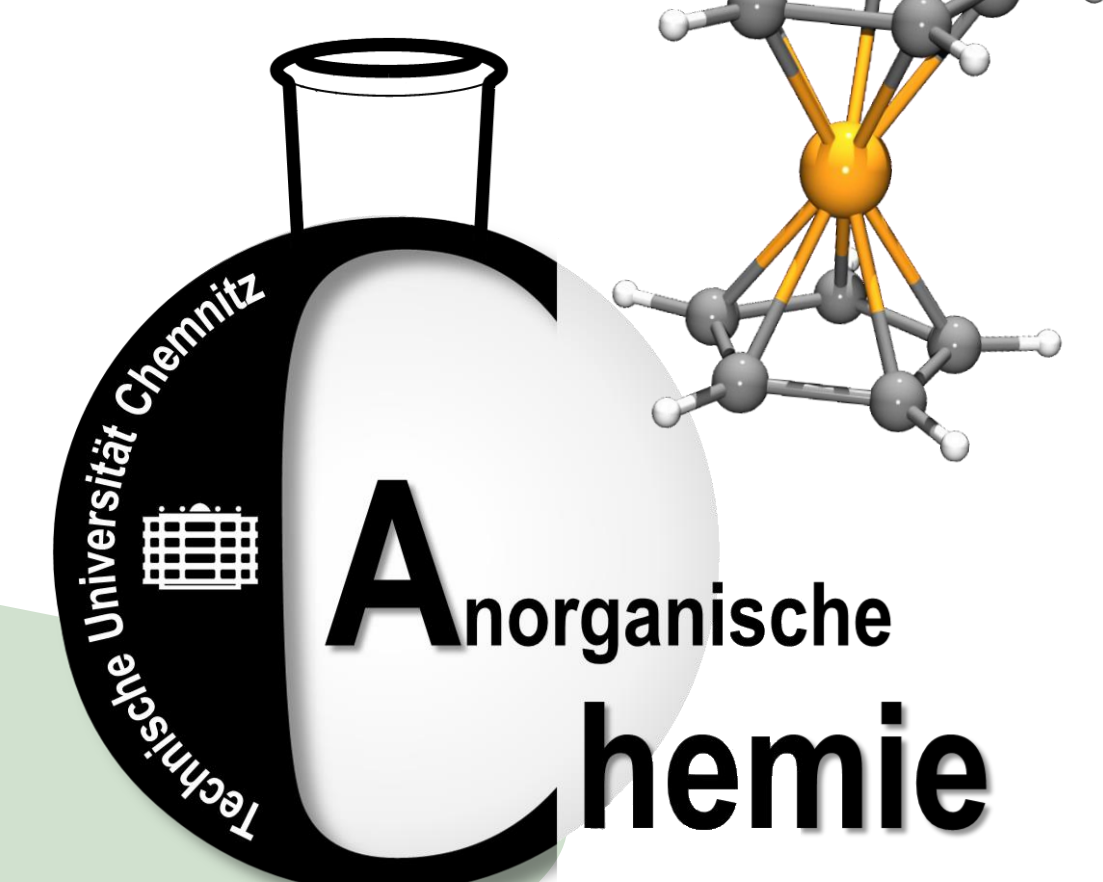


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# Synthesis, Molecular Solid-State Structures and Electrochemical Behavior of Monoarylferrocenes

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## Introduction

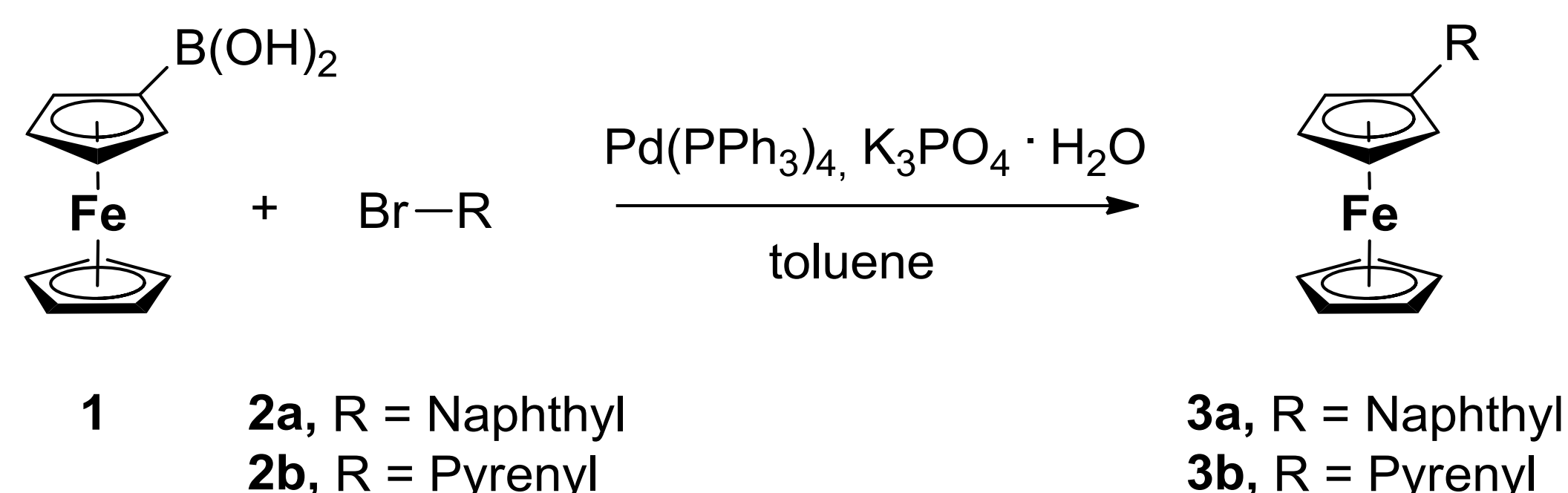
Ferrocene derivatives are widely studied due to their electron-donating ability, electrochemical reversibility<sup>[1]</sup> and, for example, the non-linear optical behavior.<sup>[2]</sup> The combination of ferrocene with aromatics, such as naphthalene and pyrene, resulted in interesting optical characteristics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

$\beta$ -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<sub>5</sub>H<sub>4</sub> building block (2.1 (4) °). Sandwich compound **3b** has a torsion angle for the substituted cyclopentadienyl unit to the pyrenyl unit of – 38.9 (3) °. The pyrenyl moiety is significant twisted against the C<sub>5</sub>H<sub>4</sub> building block of ferrocene.

## X-ray Discussion

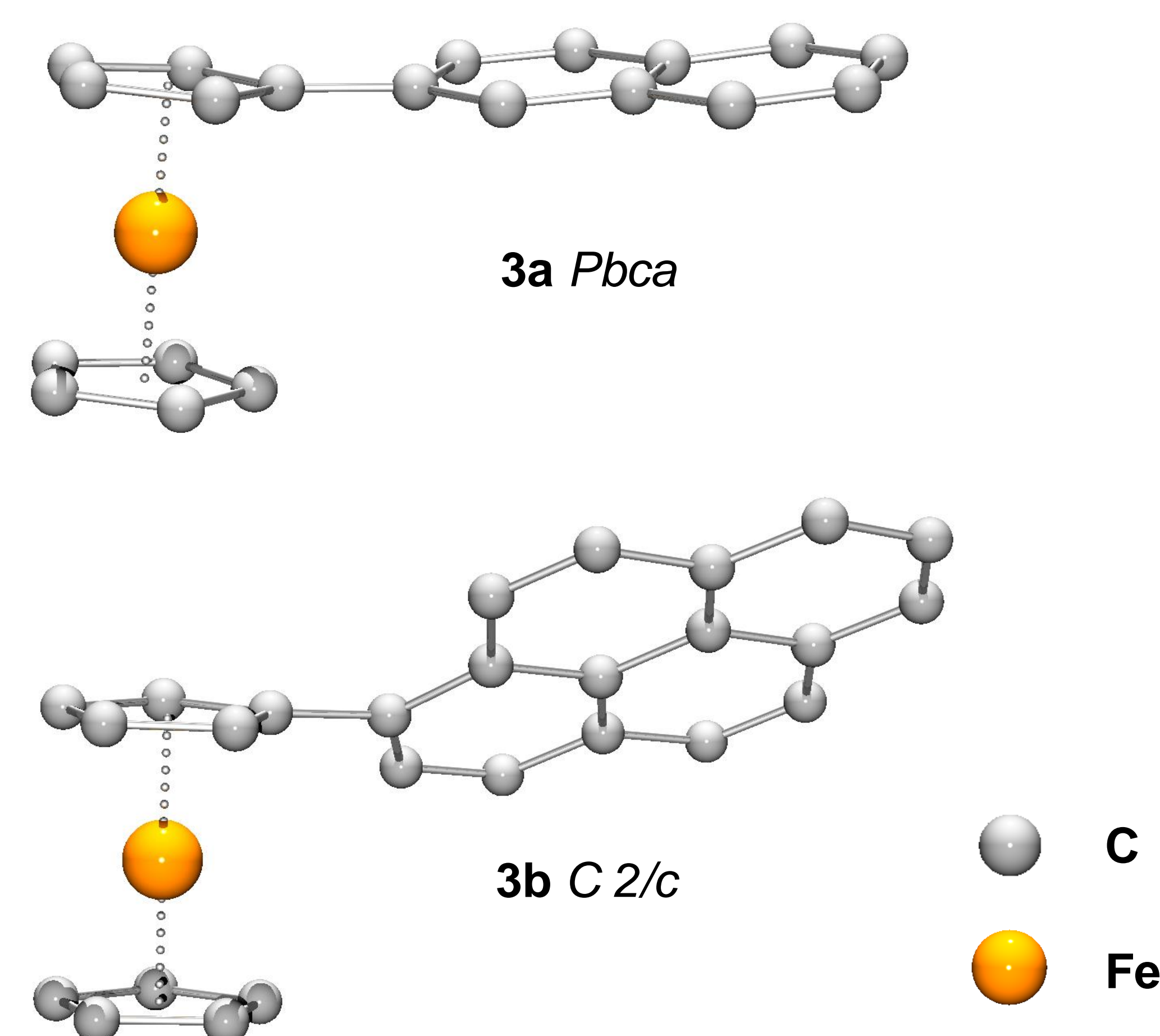


Figure 1. Solid state structure of **3a** (top) and **3b** (below).

## (Spectro)Electrochemistry

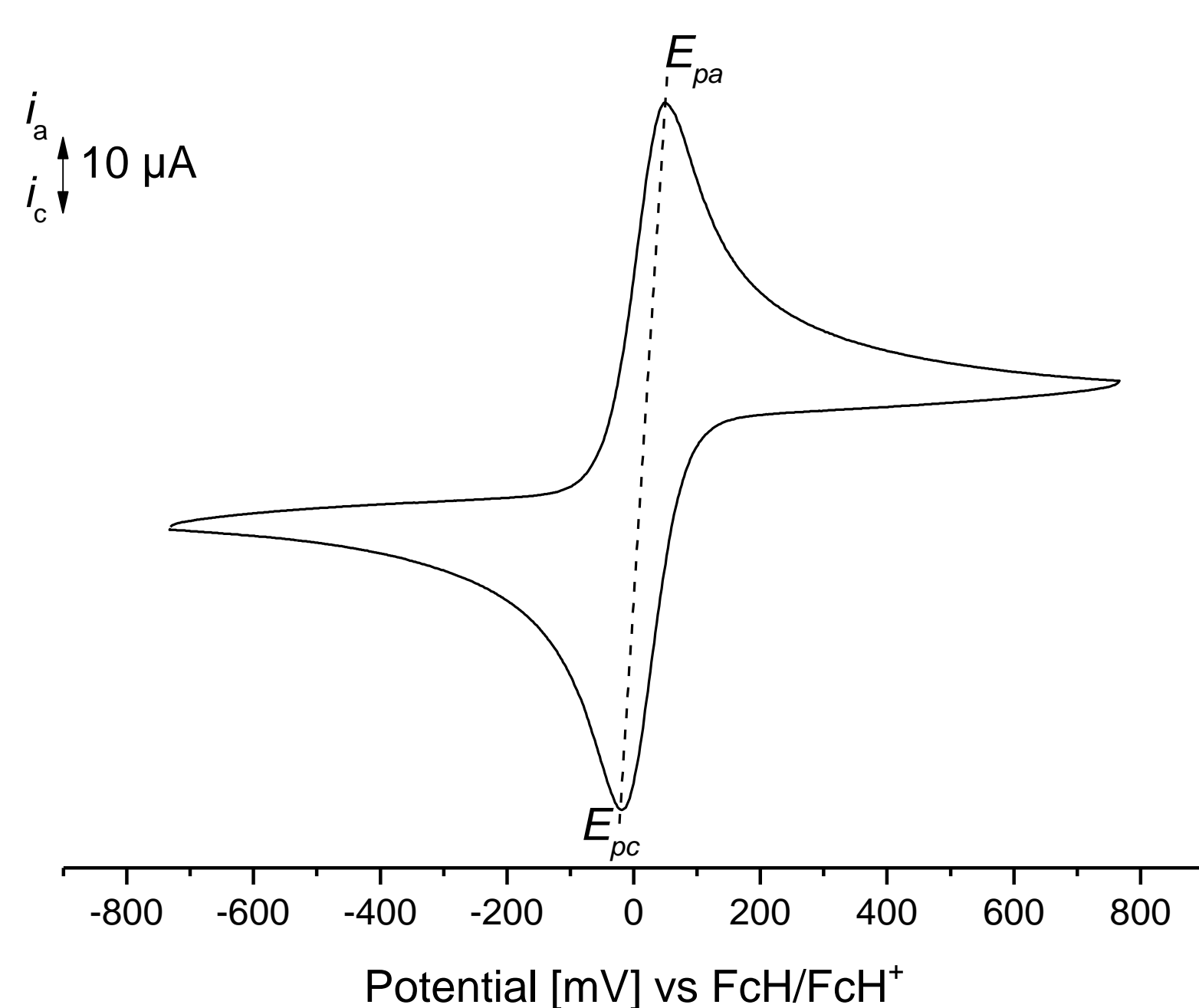


Figure 2. Cyclic voltammogram of **3a**; scan rate 100 mV · s<sup>-1</sup> at glassy carbon electrode, 1.0 mmol·L<sup>-1</sup> solution in anhydrous dichloromethane; 0.1 mmol·L<sup>-1</sup> [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte at 25 °C.

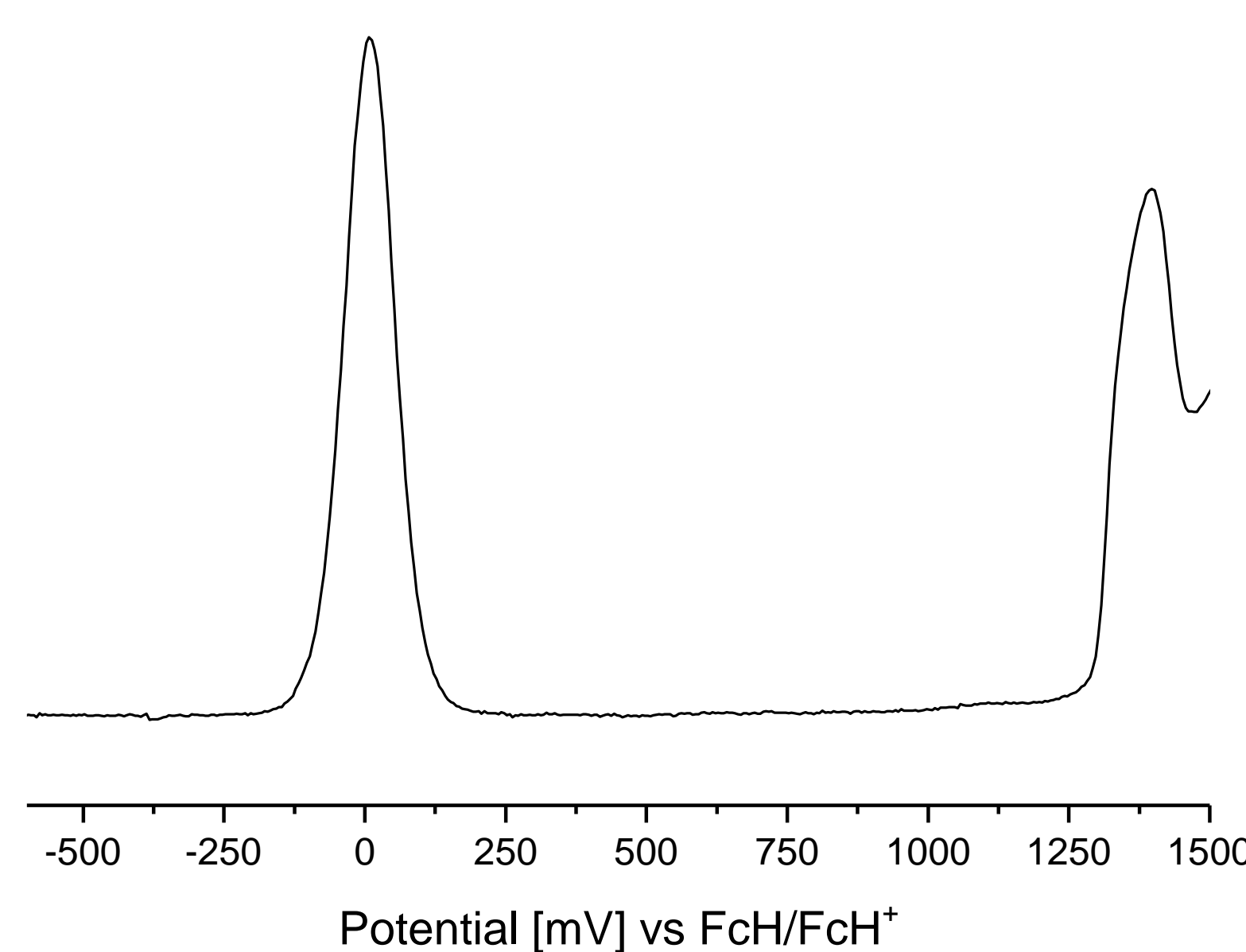


Figure 3. Square wave voltammogram of **3a**; 1.0 mmol·L<sup>-1</sup> solution in anhydrous dichloromethane; 0.1 mmol·L<sup>-1</sup> [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte at 25 °C.

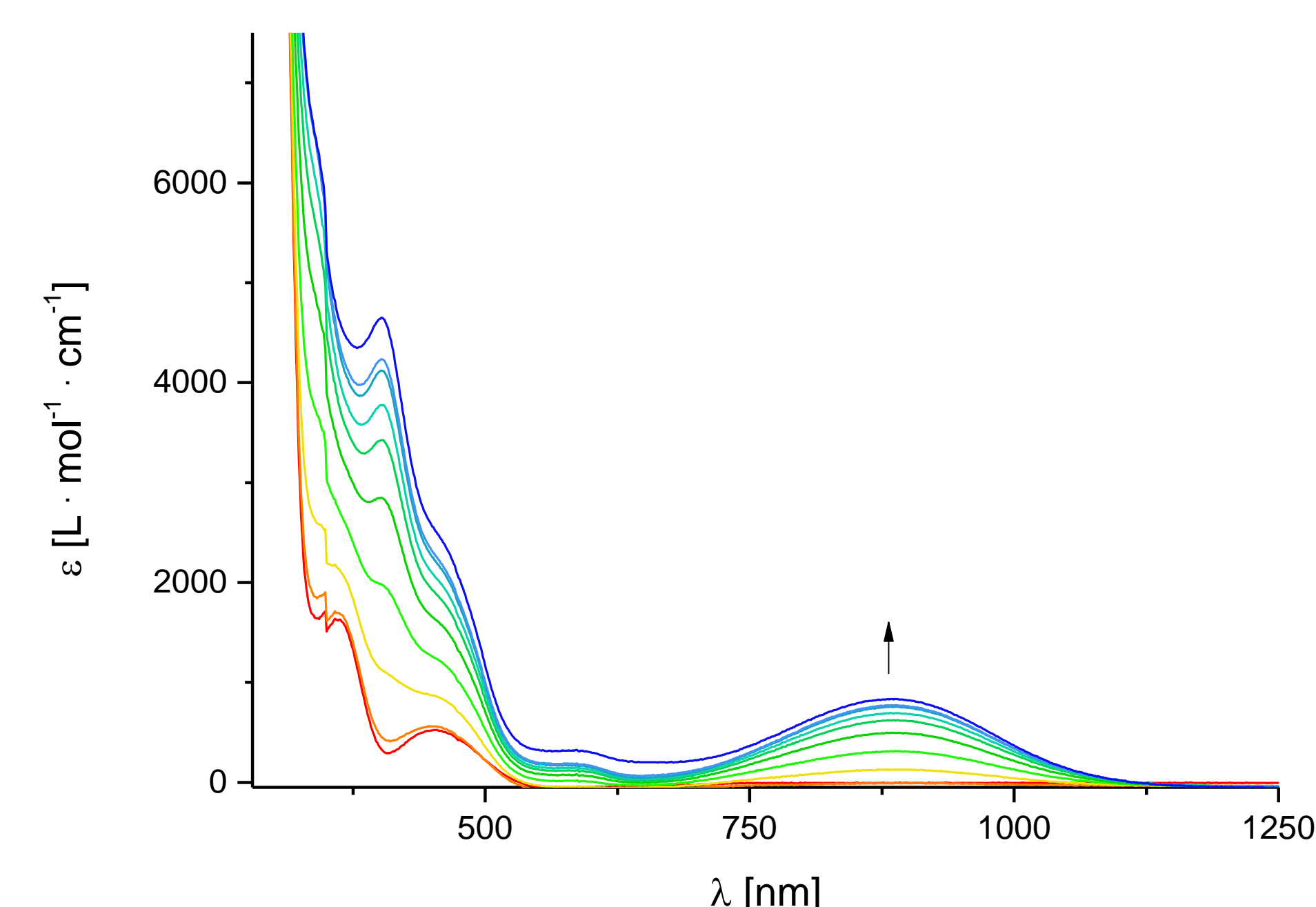


Figure 4. UV-Vis/NIR spectra of **3a** at rising potentials (100, 50, 25 mV steps) vs Ag/AgCl in an OTTE cell; measurement conditions: 25 °C, dichloromethane, 0.02 mmol·L<sup>-1</sup> [N<sup>n</sup>Bu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], arrows indicate increasing of absorptions.

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

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

<sup>a</sup> $E^{\circ'}$  = formal potential. <sup>b</sup> $\Delta E_p$  = Difference between the oxidation and the reduction potential. <sup>c</sup>Values determined with Square wave voltammetry.

The cyclic voltammogram (CV) (Figure 2) of **3a** shows one reversible redox event. With increasing size of the aryl group at ferrocene, the  $E_1^{\circ'}$  value is shifted to anodic potentials indicating that the metal centre is more difficult to oxidize. The 2<sup>nd</sup> 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 easy to oxidize 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 moiety.<sup>[3,5]</sup>

## 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  $E_1^{\circ'}$  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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