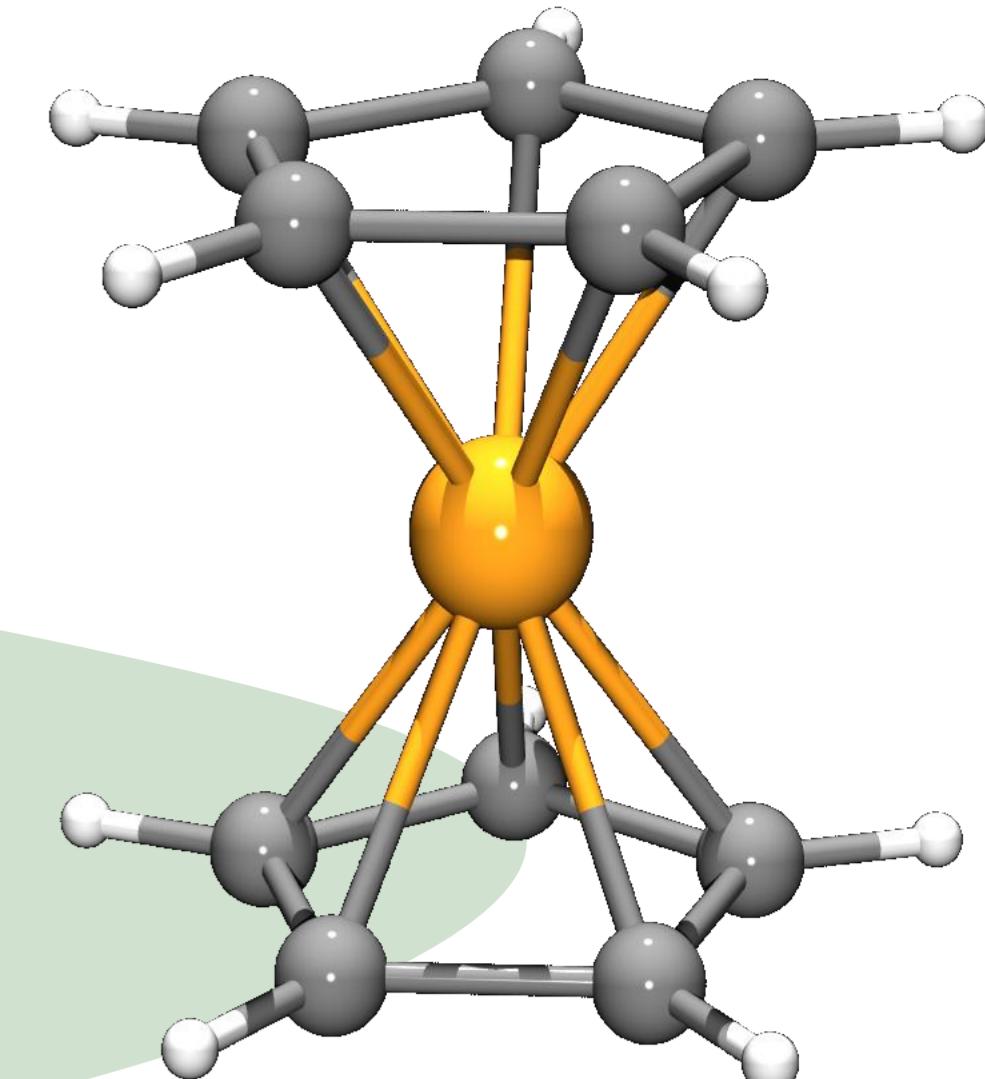


Electron Transfer Studies in *trans*-Platinum Bis(Acetylide) Complexes



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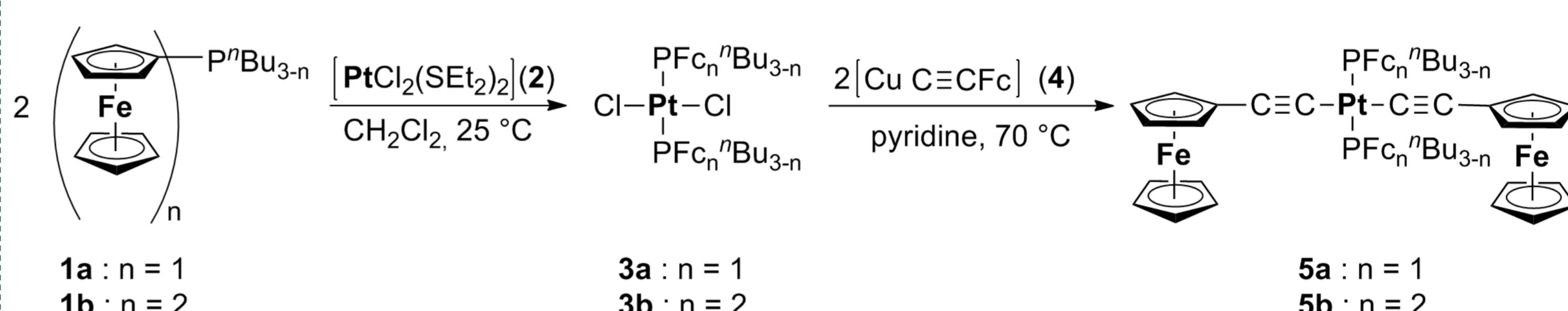
Introduction

Compounds with two redox-active transition metal fragments connected *via* carbon-rich π -conjugated spacer units have received considerable attention as they can be used for electron transfer studies and can be regarded as model compounds for molecular wires.^[1] Herein, we report on the synthesis and characterization of *trans*-platinum

bis(acetylide) complexes containing ferrocenyl units as well as their electrochemical and spectro-electrochemical behavior. Furthermore, the influence of the ferrocenyl substituents of the phosphines on the intervalence charge-transfer will be discussed.

Synthesis of *trans*-Platinum Bis(Acetylide) Complexes

The synthesis of the *trans*-platinum bis(acetylides) **5a** and **5b** is presented in Scheme 1. Reaction of two equivalents of the ferrocenylphosphines **1a** and **1b** with $[\text{PtCl}_2(\text{SEt}_2)_2]$ produced the platinum(II) chlorides **3a** and **3b** as orange colored solids. Complexes **5a** and **5b** were prepared by treatment of **3a** and **3b** with two equivalents of cuprous ferrocenylacetylide in pyridine at 70 °C.



Scheme 1. Synthesis of *trans*-platinum bis(acetylide) complexes **5a** and **5b**.

Electrochemistry

The redox properties of compounds **3a**, **3b** and **5a** - **5c** have been studied by cyclic voltammetry and were compared with the electrochemical behavior of the literature known complex *trans*- $[\text{Pt}(\text{C}\equiv\text{C}-\text{Fc})_2(\text{P}^n\text{Bu}_3)_2]$ ^[2] (**5c**). As supporting electrolyte 0.1 mol/L solutions of $[\text{N}^+\text{Bu}_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]$ in dichloromethane were used.

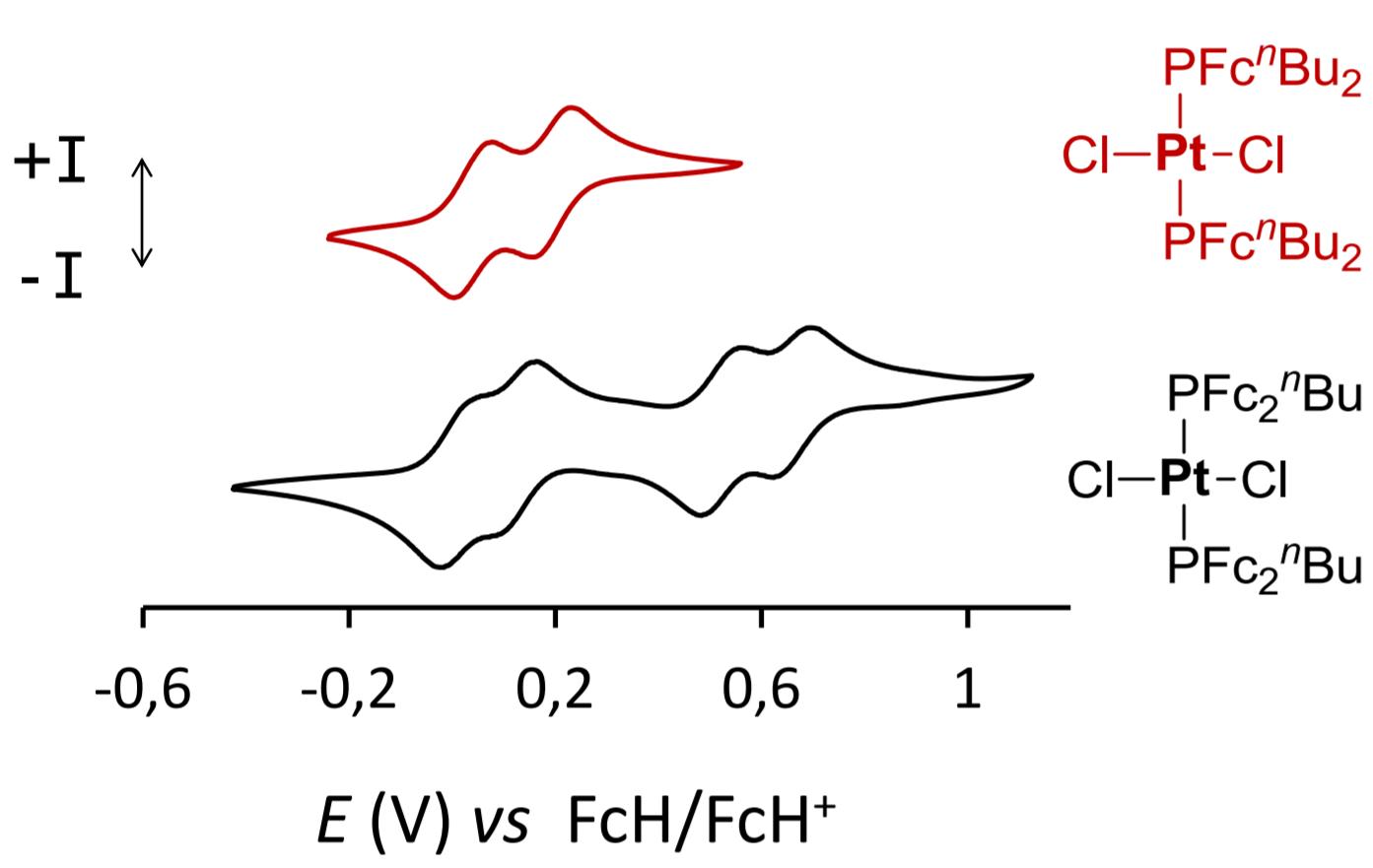


Figure 1. Cyclic voltammograms of complexes **3a** and **3b**.

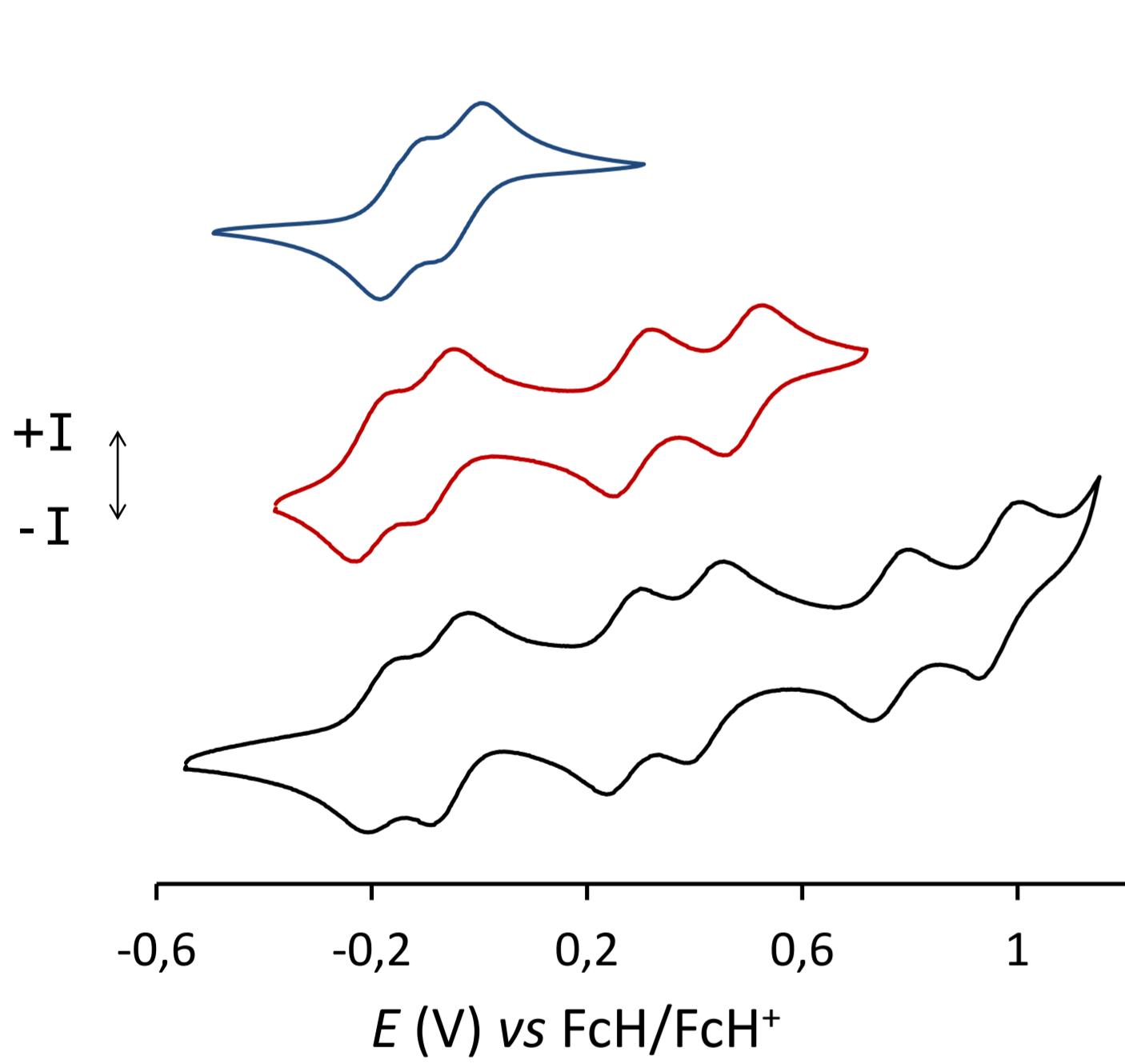


Figure 2. Cyclic voltammograms of complexes **5a** - **5c**.

Compounds **5a** - **5c** show one reversible redox process for each ferrocenyl unit. By comparison with complex **5c** the first two processes can be assigned to the ethynylferrocenyl groups. In complexes **5a** and **5b** two and four, respectively, further redox processes at higher potentials can be observed for the ferrocenyl units bonded to the phosphorus atoms. Moreover, the peak separation $\Delta E_{1/2}$ for the first two processes increases from **5c** (107 mV) to **5a** (116 mV) to **5b** (120 mV) with an increasing number of ferrocenyl units present in the phosphines. The results of the electrochemical investigations are an indication for weakly coupled class II systems according to Robin and Day.

Conclusion

A series of *trans*-platinum bis(acetylides) were synthesized and the electronic coupling between the terminated redox-active units was studied. Electrochemical investigations indicated electronic communication between the ethynylferrocenyl units. The results were confirmed by *in situ* UV/Vis-NIR measurements. No intervalence charge-transfer band could be observed for the phosphine bonded ferrocenyl groups, while a small interaction between the ethynylferrocenyl groups exists. Furthermore, it could be shown that the phosphines influence the interaction between the ethynylferrocenyl units. An increasing donor ability of the phosphines results in an increased electronic communication.

Spectro-Electrochemistry

The spectro-electrochemical measurements were performed in an OTTLE (= Optically Transparent Thin-Layer Electrode) cell by stepwise increasing the potentials from -100 to 1300 mV that contained dichloromethane solutions of complexes **3a**, **3b**, **5a** and **5b** (1.0 mM) and $[\text{N}^+\text{Bu}_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]$ (0.1 M) as supporting electrolyte.

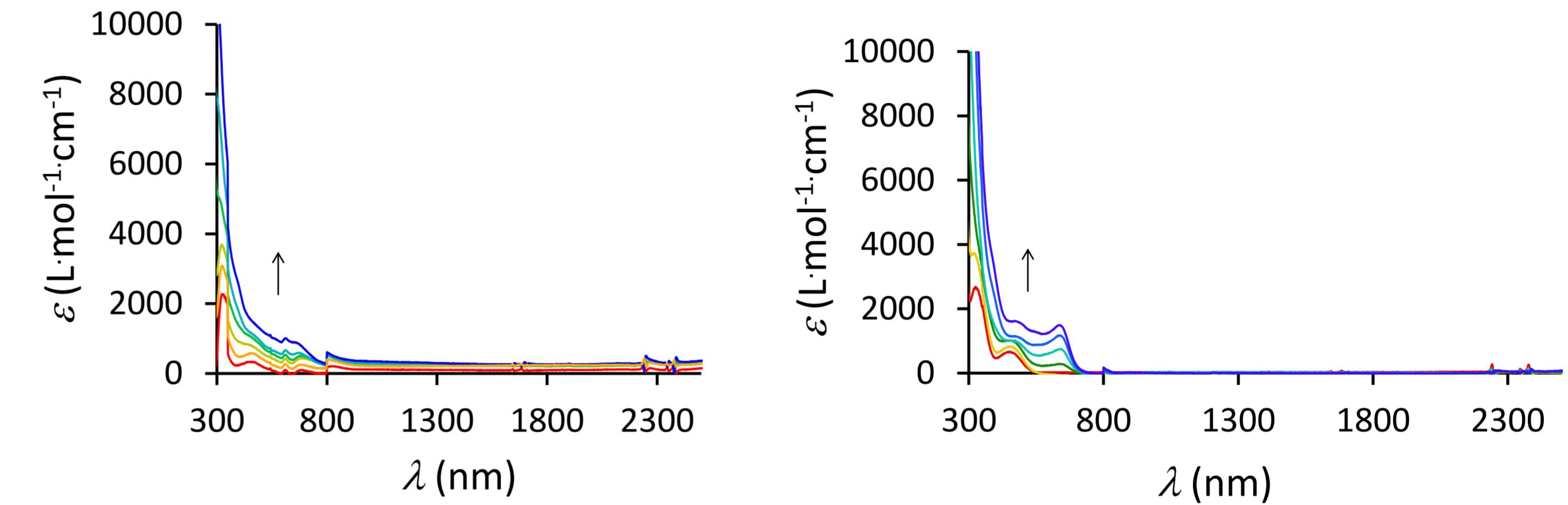


Figure 3. NIR spectra of **3a** (left) and **3b** (right) at rising potentials (**3a**: -100 – 1300 mV; **3b**: -200 – 1200 mV vs Ag/AgCl).

During the oxidation of **3a** and **3b**, respectively, no intervalence charge-transfer absorptions could be observed in the near infra red. No electronic interaction exists in these complexes between the ferrocenyl units bonded on the phosphorus atom. Based on these results, the interactions are most likely of electrostatic nature.

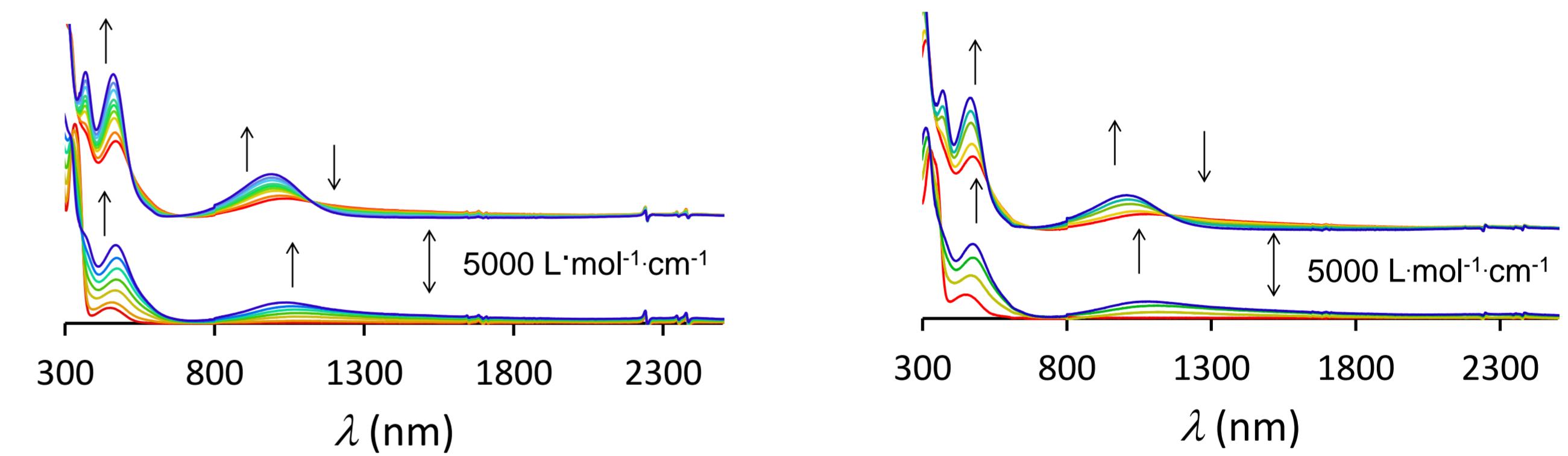


Figure 4. Left: NIR spectra of **5a** at rising potentials (bottom: 0 – 500 mV; top: 500 – 1200 mV vs Ag/AgCl); right: NIR spectra of **5b** at rising potentials (bottom: 250 – 450 mV; top: 450 – 1200 mV vs Ag/AgCl).

Molecules **5a** and **5b** show one absorption during the oxidation, which steadily increases and a second absorption, which decreases after reaching a maximum at 500 mV (**5a**) and 450 mV (**5b**), respectively. After deconvolution, the first absorption at 1000 nm can be assigned to a ligand-to-metal charge-transfer and the second at 1200 – 1400 nm to an intervalence charge-transfer process. On account of the small intensities (**5a**: 293 L·mol⁻¹·cm⁻¹, **5b**: 324 L·mol⁻¹·cm⁻¹) and the large bandwidth-at-half-height values of the IVCT absorptions (~2500 cm⁻¹), a classification in weakly coupled class II systems according to Robin and Day can be made. Furthermore, it could be shown that an increasing number of ferrocenyl units bonded on phosphorus (decreased donor properties) resulted in a decreasing electronic coupling between the ethynylferrocenyl groups.

References and Acknowledgement

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