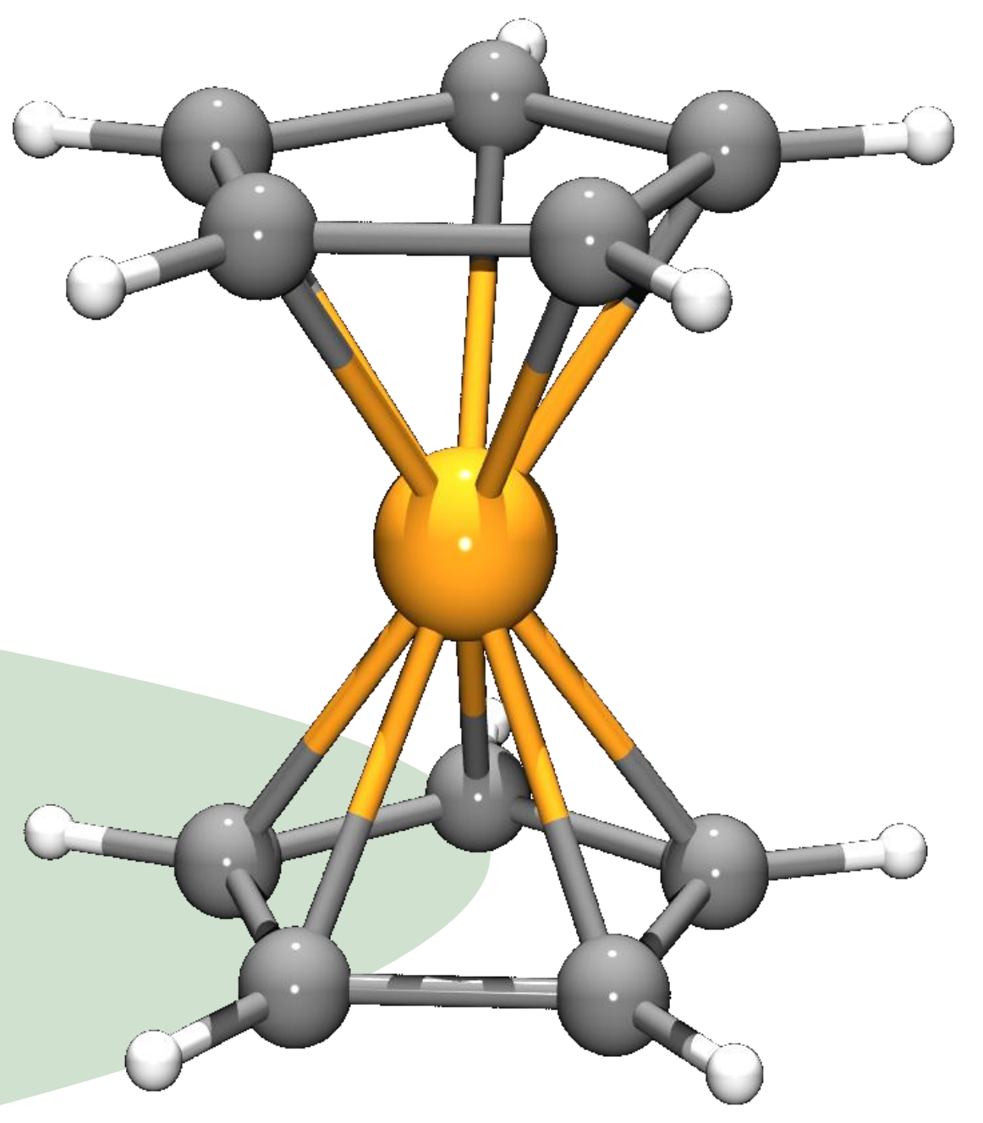
# Synthesis, Electrochemistry and Spectro-electrochemistry of 2,5-Diferrocenyl-1-phenyl-1*H*-phoshpole



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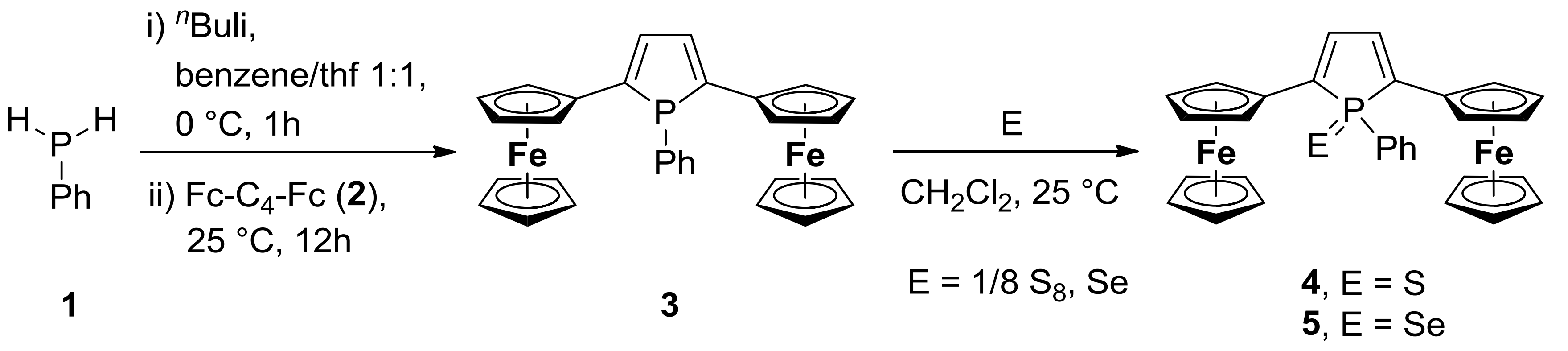
## Introduction

Compounds with two redox-active transition metal fragments connected *via* a $\pi$-conjugated unit are of considerable interest as they can be used for electron transfer studies and can be regarded as models for molecular wires.[1] In the past, a good interaction between the redox-active end-groups could be achieved using heterocycles, *e.g.* pyrroles as bridging units.[2] 2,5-Diferrocenyl- and 2,3,4,5-tetraferrocenyl-substituted furans, thiophenes and pyrroles have successfully been applied in electron transfer studies.[3] To enrich this family of compounds, we synthesized electronically and chemically interesting phosphole molecules and report on their electrochemical and spectroelectrochemical behavior.

## Synthesis of 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole

The synthesis of 2,5-diferrocenyl-1-phenyl-1*H*-phosphole (**3**) and the corresponding sulfide and selenide is presented in Scheme 1. Phosphole **3** has been successfully prepared by reaction of phenylphosphine (**1**) with *n*-butyllithium und following treatment with 1,4-diferrocenylbutadiyne (**2**). Subsequent reaction with elemental sulfur or selenium, respectively, leads to the formation of the phosphole sulfide (**4**) and selenide (**5**).



**Scheme 1**. Synthesis of phospholes **3** – **5**, Fc = **Fe**($\eta^5$-C$_5$H$_5$)($\eta^5$-C$_5$H$_4$).

## Electrochemistry

The redox properties of heterocycles **3** – **5** have been studied by cyclic voltammetry and square wave voltammetry. The data of the cyclic voltammetry experiments are summarized in Table 1. As supporting electrolyte 0.1 mol·L$^{-1}$ solutions of [N$^n$Bu$_4$][B(C$_6$F$_5$)$_4$] in dichloromethane were used.

**Table 1**. Cyclic voltammetry data.

| Compd. | $E^{\circ}{}_1{}'$ in mV ($\Delta E_p$ in mV) | $E^{\circ}{}_2{}'$ in mV ($\Delta E_p$ in mV) | $\Delta E^{\circ\prime}$ in mV |
|---|---|---|---|
| **3** | -110 (72) | 170 (80) | 280 |
| **4** | -15 (68) | 225 (74) | 240 |
| **5** | -15 (74) | 220 (80) | 235 |

As shown in Figure 1, the ferrocenyl groups of compounds **3** – **5** could be oxidized separately showing two reversible redox events between -110 and 225 mV. The separation of the two events, $\Delta E^{\circ\prime}$, is 280 mV (**3**), 240 mV (**4**) and 235 mV (**5**). Due to the oxidation of the phosphorous atom, the P(V) species **4** and **5** are more electron poor, which leads to a shift of the $E^{\circ\prime}$ values to higher potentials and a decreased redox splitting. The results of the electrochemical measurements are an indication for weakly to moderate coupled class II systems according to Robin and Day.[4]

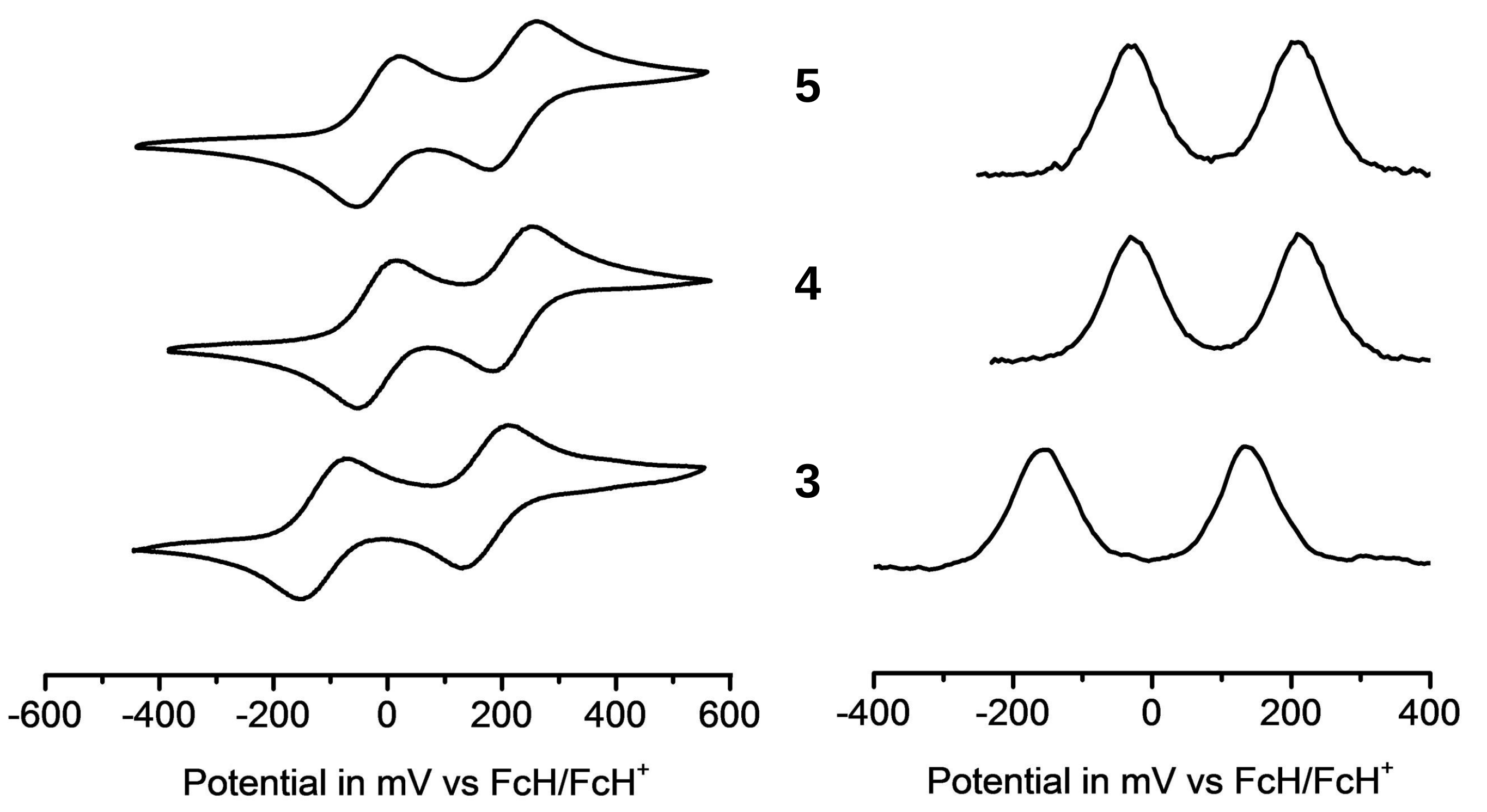


**Figure 1**. Left: Cyclic voltammograms of **3** – **5**. Right: Square wave voltammograms of **3** – **5** in dichloromethane solutions (1.0 mmol·L$^{-1}$) at 20 °C.

## Spectroelectrochemistry

The UV-vis/NIR spectroelectrochemical measurements of dichloromethane solutions containing **3** – **5** and [N$^n$Bu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte were performed in an OTTLE (OTTLE = Optically Transparent Thin-Layer Electrochemical) cell by stepwise increasing the potentials from -200 mV to 800 mV. Selenide **5** shows a similar behavior as sulfide **4**. Upon oxidation a broad band between 1500 and 2500 nm appears. A further potential increase leads to the disappearance of these absorptions, a behavior typical for intervalence charge transfer (IVCT) excitations. The observed spectra can be deconvoluted into three Gaussian-shaped bands. The sum of these three Gaussian functions allows an almost exact overlay with the experimental spectra. The blue curves represent the IVCT absorptions. Therefore, the intensity $\varepsilon_{max}$, the full-width-at-half-height $\Delta\nu_{1/2}$ and the $\nu_{max}$ values could be determined. Analysis of the IVCT absorption allows to classify **3** as a moderately coupled class II system according to Robin and Day.[4] The IVCT absorptions of sulfide **4** and selenide **5** show smaller intensities and larger $\Delta\nu_{1/2}$-values. This indicates that the occupation of the lone pair decreases the intermetallic interaction among the $^c$C$_4$P ring and characterizes those two molecules as weak class II compounds.

**Table 2**. NIR data of phospholes [**3**]$^+$ – [**5**]$^+$.

| Compd. | $\nu_{max}$ (cm$^{-1}$) ($\varepsilon_{max}$ (L·mol$^{-1}$·cm$^{-1}$)) | $\Delta\nu_{1/2}$ (cm$^{-1}$) |
|---|---|---|
| **[3]$^+$** | 5000 (1750) | 3050 |
| **[4]$^+$** | 4900 (1300) | 4200 |
| **[5]$^+$** | 4850 (1100) | 4200 |

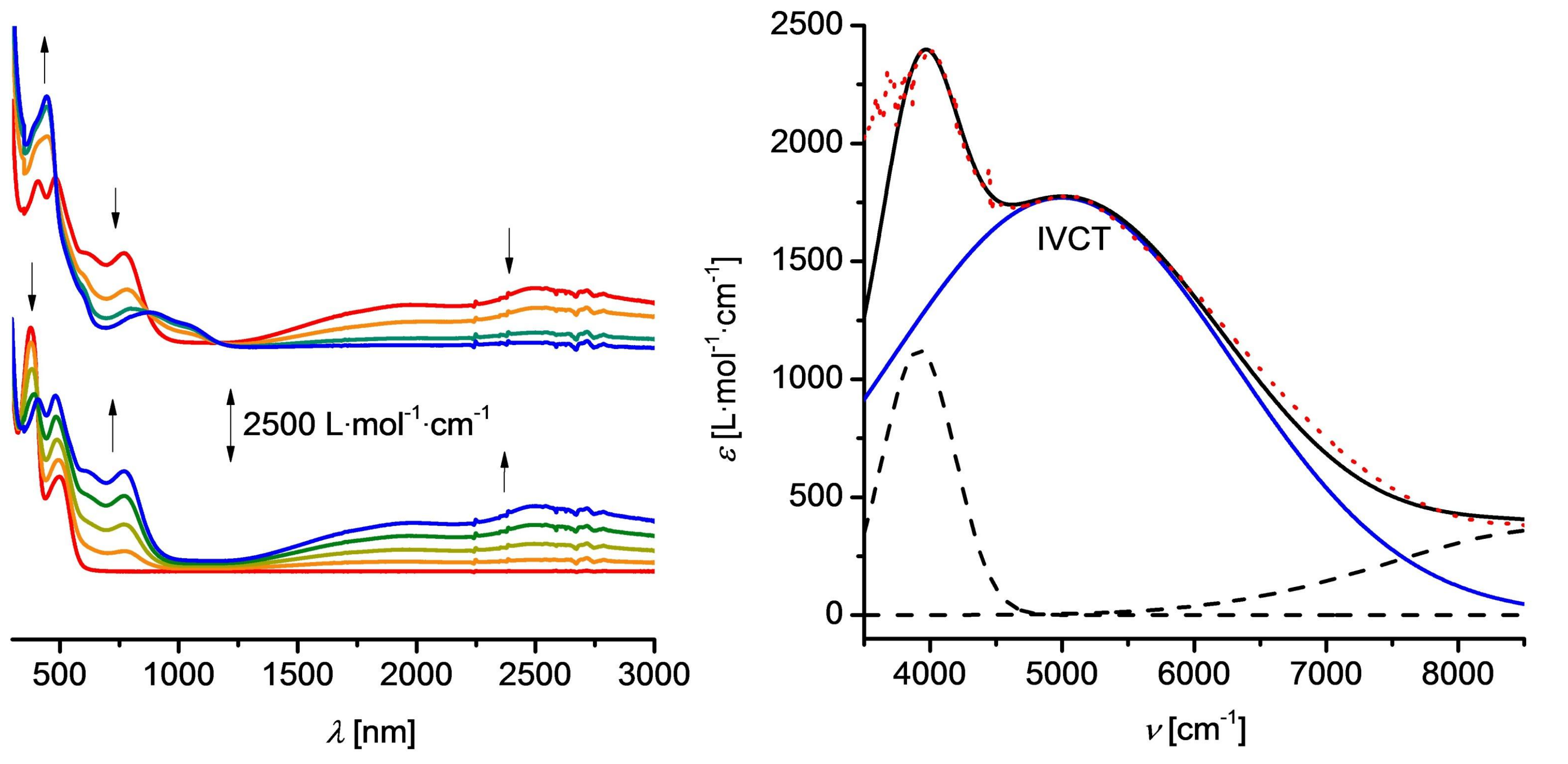


**Figure 2**. Left: UV-vis/NIR spectra of **3** at rising potentials. Right: Deconvolution of the NIR absorptions of **3$^+$**.

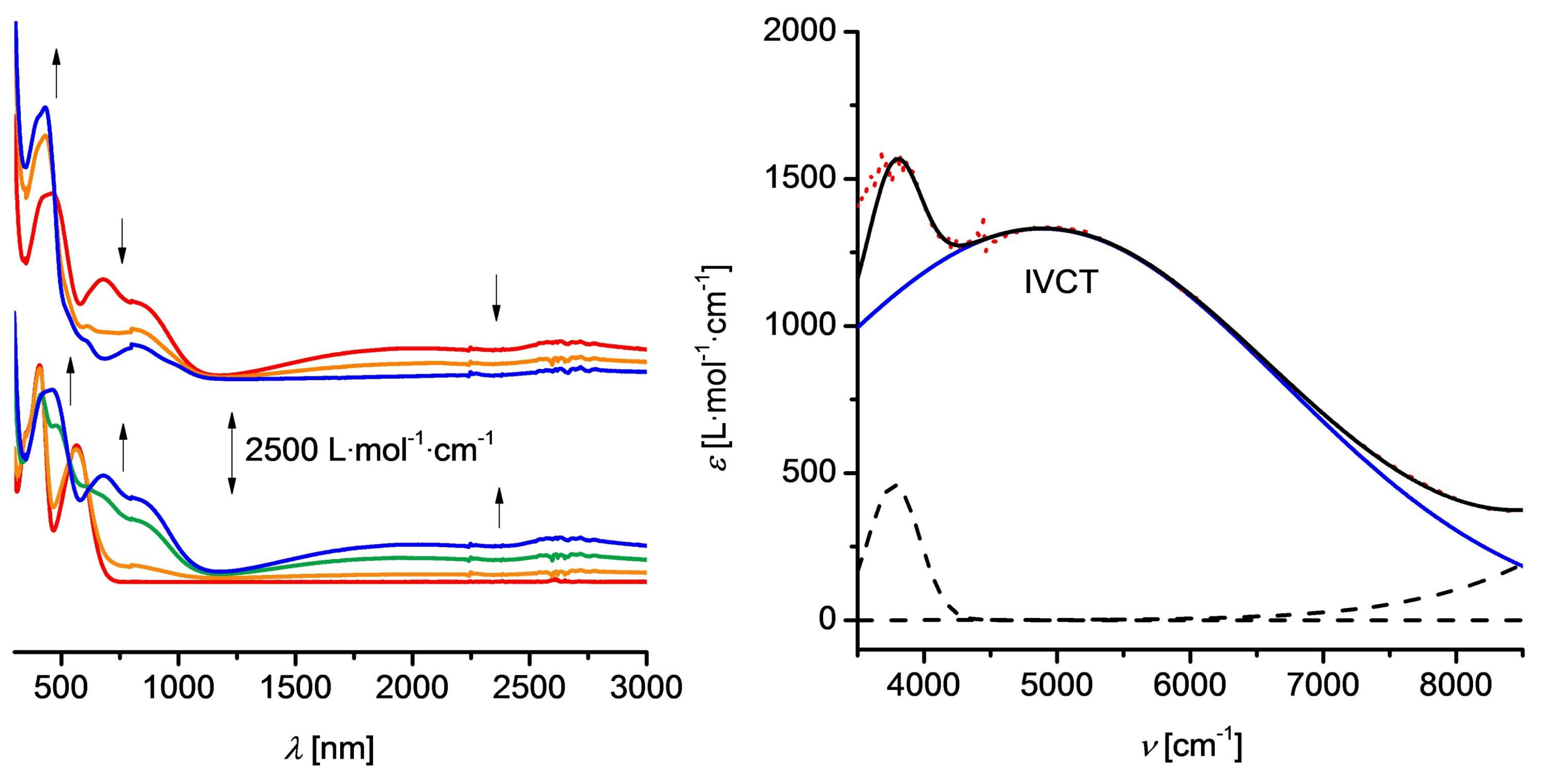


**Figure 3**. Left: UV-vis/NIR spectra of **4** at rising potentials. Right: Deconvolution of the NIR absorptions of **4$^+$**.

## Conclusion

2,5-Diferrocenyl-1-phenyl-1*H*-phosphole (**3**) and the corresponding chalcogenides **4** (P=S) and **5** (P=Se) have been successfully prepared by a cyclization reaction and subsequent reaction with sulfur and selenium, respectively. Electrochemical measurements revealed a separate oxidation of the two ferrocenyl groups in **3** – **5**, which indicates an electronic interaction between the ferrocenyl termini. These results were confirmed by UV-vis/NIR measurements. All three compounds **3** – **5** exhibit IVCT absorptions of weak to moderate strength. Due to the oxidation of P(III) to P(V) the intensity of the IVCT absorption decreases while the band broadens. This indicates that with blocking the phosphorous' lone pair the electronic communication decreases.

## References and Acknowledgement

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