

Di(biferrocenyl)ethyne and -butadiyne

Elisabeth A. Poppitz, Alexander Hildebrandt,
Marcus Korb and Heinrich Lang*

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

Introduction

Within the field of electronics one major aspect is to minimize the electronic gate distance for transistors in order to maximize the number of logical units per area. [1] In this respect, single molecules can be used as functional units within an electronic

device and hence the (spectro)electrochemical properties of di(biferrocenyl) ethyne and -butadiyne have been investigated revealing electron transfer interactions between the ferrocenyl / ferrocenium units within the mixed-valent species. [2]

Synthesis

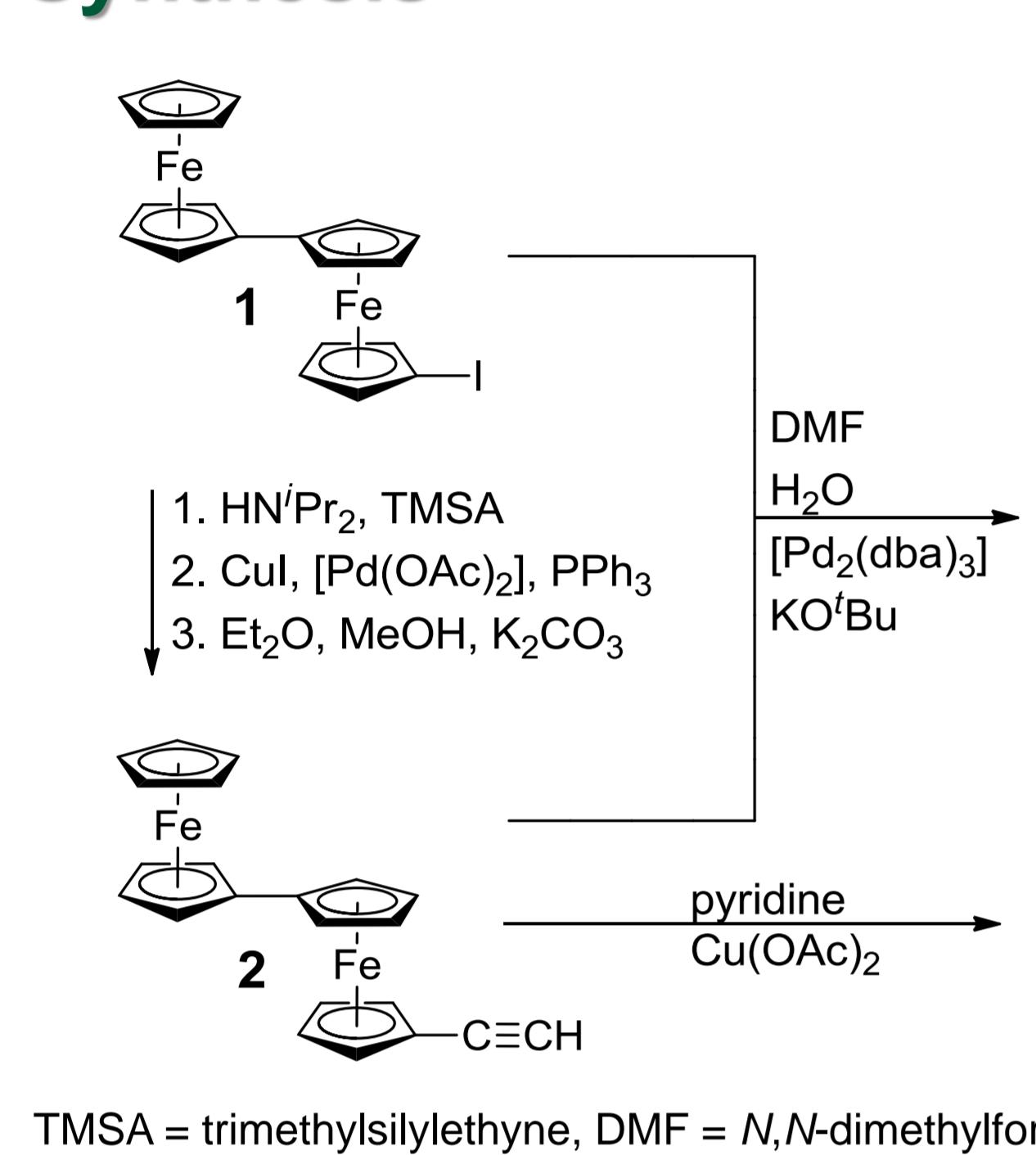


Figure 1. Synthesis of 2 – 4. ORTEP diagram (50 % probability level) of the molecular structure of 4.

Spectroelectrochemistry

Compd.	ν_{max} (cm ⁻¹) (ϵ_{max} (L·mol ⁻¹ ·cm ⁻¹))	$\Delta\nu_{1/2}$ (cm ⁻¹)	$(\Delta\nu_{1/2})_{\text{theo}}^{\text{a)}$ (cm ⁻¹)
3 ⁺	5000 (3000)	3500	3400
3 ²⁺	5000 (1250)	3450	3400
3 ³⁺	5300 (1100)	3950	3500
4 ²⁺	5300 (1800)	3500	3500
4 ³⁺	5700 (1100)	3900	3630

a) Values calculated as $(\Delta\nu_{1/2})_{\text{theo}} = (2310 \cdot \nu_{\text{max}})^{1/2}$ according to the Hush relationship for weakly coupled systems. [3]

The observed IVCT transitions of 3 and 4 in any mixed-valent oxidation state allowed the characterization of these species as class II systems according to Robin and Day. [4]

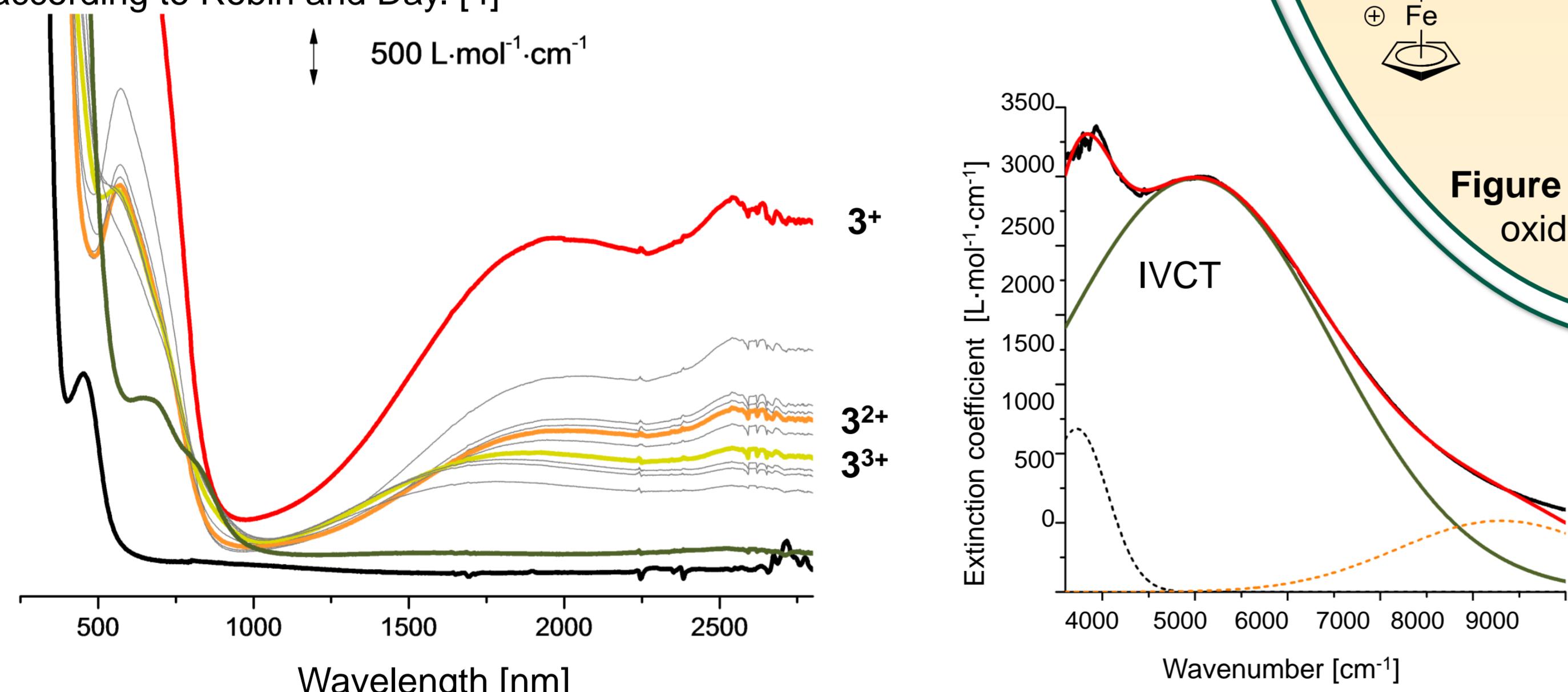


Figure 3. UV-Vis/NIR spectra of 3⁺ (n = 1, 2, 3) (left) at 20 °C in dichloromethane (2.0 mmol·L⁻¹) at rising potentials (supporting electrolyte $[\text{N}^{\text{v}}\text{Bu}_4]\text{B}(\text{C}_6\text{F}_5)_4$). Deconvolution of the NIR absorptions of 3⁺ (right).

Conclusion

Di(biferrocenyl)ethyne and -butadiyne have been prepared by Sonogashira and Eglinton C,C cross-coupling reaction protocols. Based on the research criteria and with the aid of the results of the (spectro)electrochemical measurements the mechanism of the oxidation of 3 – 4 could be clarified. It could be shown that all four ferrocenyl units can reversibly be oxidized and that the peripheral ferrocenyls of the bfc moieties are oxidized at first simultaneously followed by a separate oxidation of the fc units connected to the $(-\text{C}\equiv\text{C})_n$ ($n = 1, 2$) bridges. The individual redox separations resemble literature known values for biferrocene (difference between 1st and 2nd process) and difterrocenyl ethyne or -butadiyne (difference between 2nd and 3rd process), respectively. Therefore, the electronic interaction is limited to the ferrocenyls directly attached to the spacer unit and is similar to the appropriate ferrocenyl analogs.

Electrochemistry

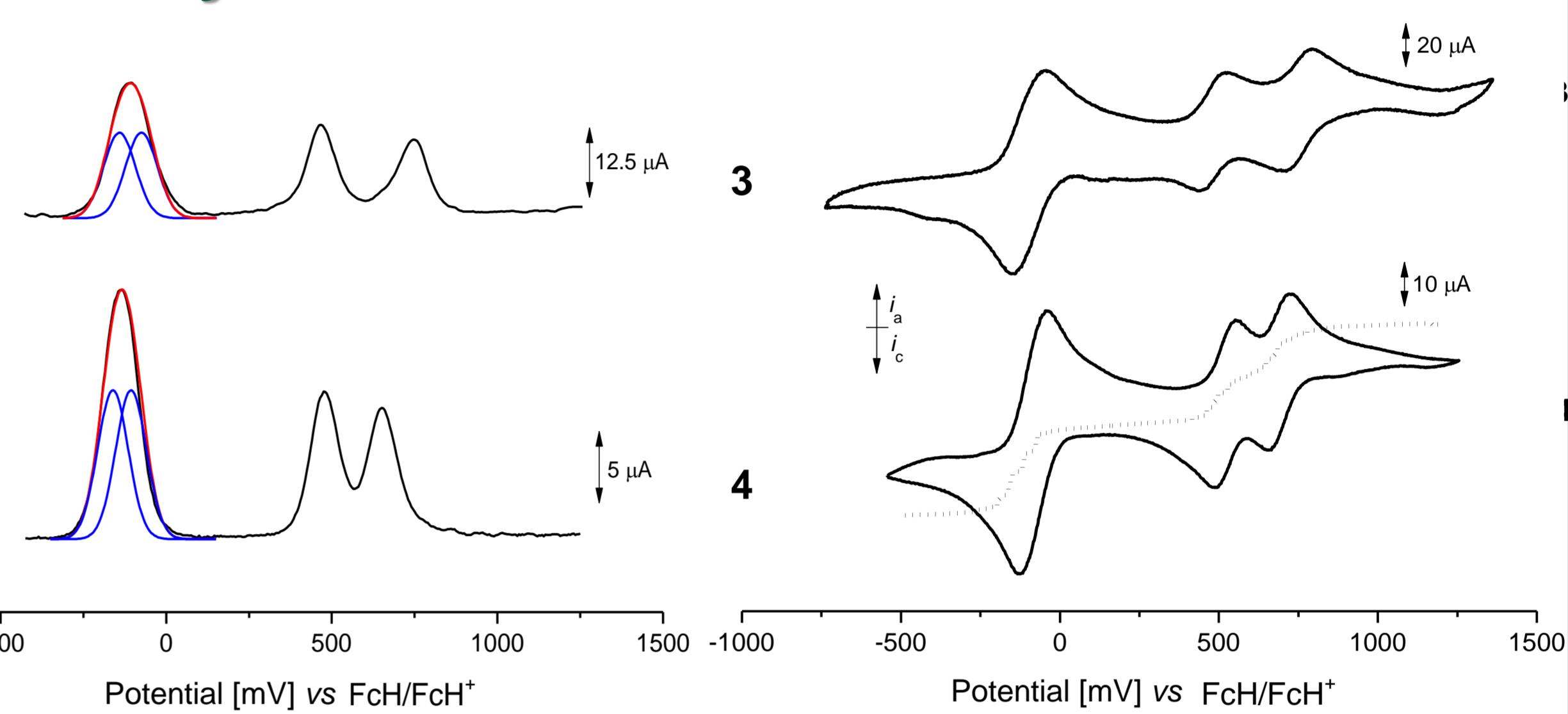


Figure 2. Left: Square wave voltammograms of 3 – 4. Right: Cyclic voltammograms of 3 – 4 and linear sweep voltammogram of 4 (1.0 mmol·L⁻¹ dichloromethane solutions, 20 °C, supporting electrolyte 0.1 mmol·L⁻¹ $[\text{N}^{\text{v}}\text{Bu}_4]\text{B}(\text{C}_6\text{F}_5)_4$, glassy carbon working electrode (surface area 0.031 cm²)).

Compd.	$E^{\circ 1}$ in mV (ΔE_p in mV)	$E^{\circ 2}$ in mV (ΔE_p in mV)	$E^{\circ 3}$ in mV (ΔE_p in mV)	ΔE° in mV
3	-95 (94)	490 (73)	755 (76)	585/265
4	-85 (80)	520 (74)	685 (67)	605/165

For both compounds three reversible ferrocene-related redox processes could be observed. The relative currents of these redox events indicated that the 1st process is consistent of a simultaneous oxidation of the two terminal ferrocenyl (fc) groups of the biferrocenyl (bfc) entities, while the 2nd and the 3rd event represent a subsequent one-electron oxidation of the two remaining inner ferrocenyl units. As expected, the redox splitting between the 2nd and 3rd process decreases by increasing the length of the carbon-rich connectivity. [5]

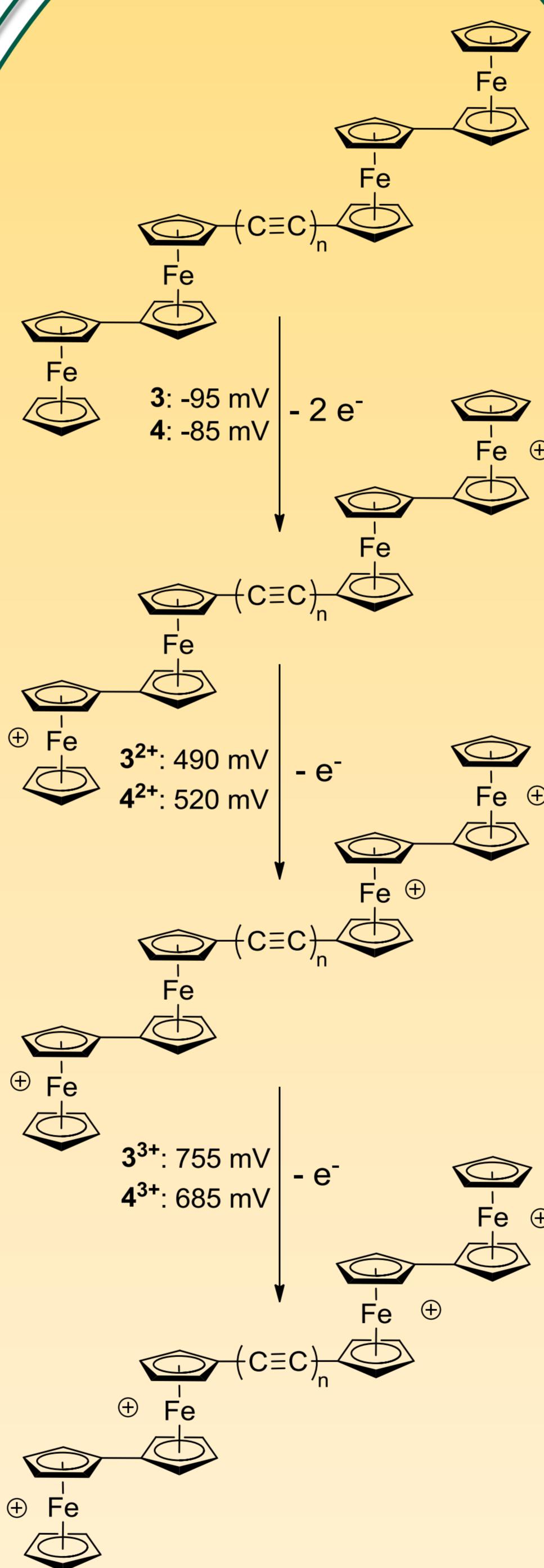


Figure 4. Electrochemical oxidation of 3 and 4.

Within *in situ* IR spectroscopy, 3^{3/4+} showed two $\nu_{\text{C=C}}$ stretching vibrations, due to Fermi resonance, while for 4^{3/4+} only one band was observed.

IR spectroscopy

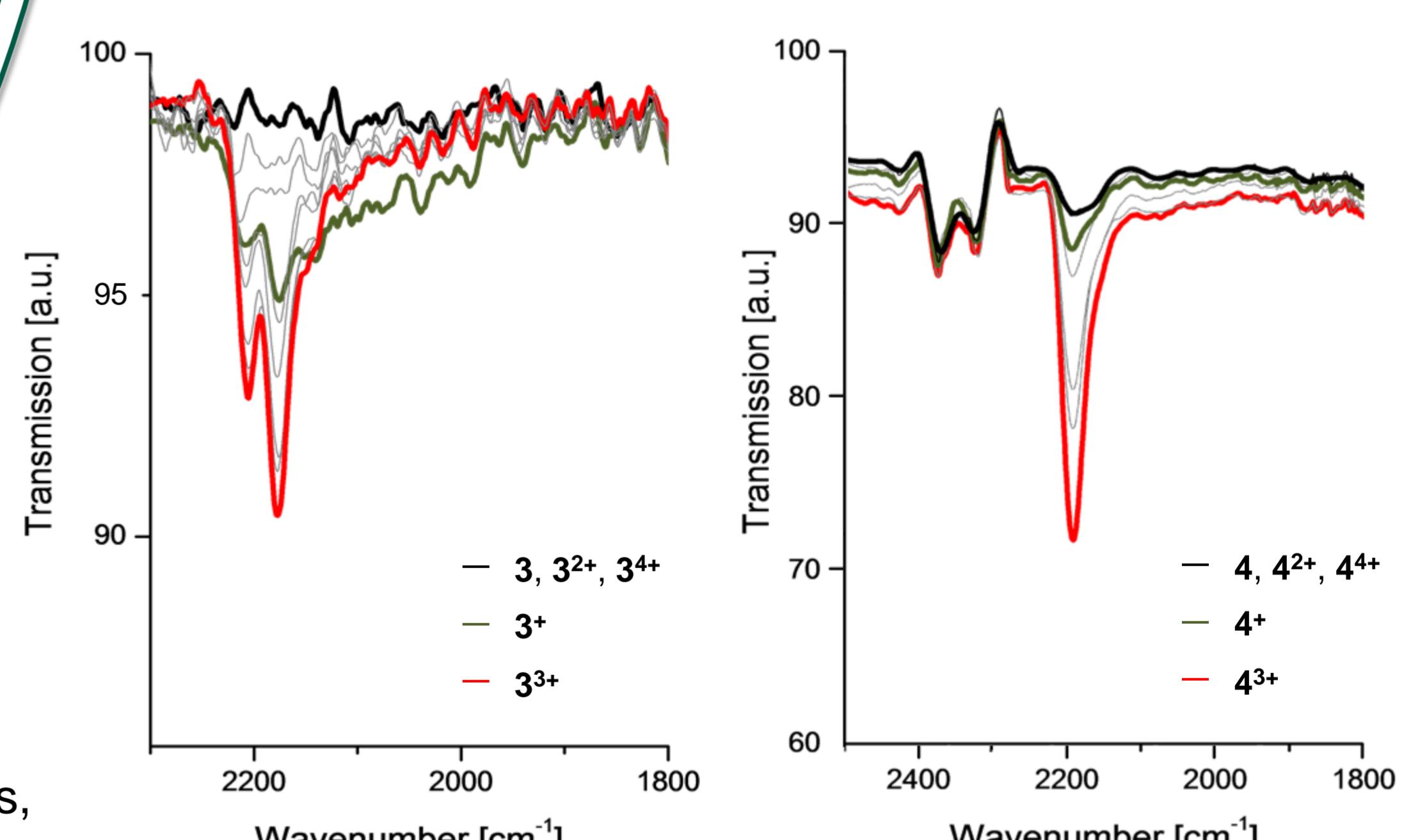


Figure 5. Left: IR spectra of 3 during electrochemical oxidation to 3⁴⁺. Right: IR spectra of 4 during electrochemical oxidation to 4⁴⁺ at 20 °C in dichloromethane (10.0 mmol·L⁻¹), supporting electrolyte $[\text{N}^{\text{v}}\text{Bu}_4]\text{B}(\text{C}_6\text{F}_5)_4$.

References and Acknowledgement

- J.K. Gimzewski, C. Joachim *Science* **1999**, 283, 1683 – 1688.
- a) L.A. Hore, C.J. McAdam, J. Simpson *Organometallics* **2000**, 19, 5039 – 5048.
b) M. Lohan, P. Ecorchard, T. Rüffer, F. Justaud, C. Lapinte, H. Lang *Organometallics* **2009**, 28, 1878 – 1890.
- N.S. Hush, *Electrochim. Acta* **1968**, 13, 1005 – 1023.
- M.B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, 10, 247 – 422.
- E.A. Poppitz, A. Hildebrandt, M. Korb, H. Lang *J. Organomet. Chem.* **2014**, 752, 133 – 140.

We are grateful to the Deutsche Forschungsgemeinschaft (cluster of excellence EXC1075, MERGE) for generous financial support. M.K. thanks the Fonds der Chemischen Industrie for a Chemiefonds fellowship.