Introduction

Electron transfer (ET) within the mixed-valent complexes has attracted scientific attention during recent years.[1] Within the work presented here, the effect of variant electron density at the iron atoms on the ET within substituted biferrocenes is investigated. Biferrocenes have been among the first mixed valent species and thus have been thoroughly studied. While steric influences on the electron transfer properties are well described, a systemic analysis of electronic changes within mixed-valent biferrocenes has not been documented this far.

Synthesis

In this work, a series of substituted biferrocenes 1 - 5 was studied. Compound 3 and 4 were synthesized stepwise by a palladium-catalyzed Negishi Cu,C-coupling reaction from dibromoferrocene, while dialkyl- (1) and dicyno-substituted biferrocene (5) were prepared in a one-step reaction from 4, respectively. Diiodobiferrocone (2) was obtained from the iodation of ferrocene.

The electron transfer properties of this series of molecules were studied by electro- (CV - SWV) and spectroelectrochemistry (in-situ UV/Vis/NIR measurements).

(Spectro)Electrochemistry

Within the electrochemical measurements, the effect of the electron withdrawing functionalities on the electron density at the iron atoms is reflected by an anodic shift of the 1st ferrocene based redox potential. Further more measurements in different electrolytes allowed for the evaluation of electrostatic stabilization effects of the mixed valent complexes 1 - 5 (\(\Delta \Delta E^{\text{a}}\)). The \(\Delta \Delta E^{\text{a}}\) values showed that the electrostatic repulsion in electron poor 4* and 5* is more pronounced than in the iodo derivative 2*.

Conclusion

The oscillator strength of the IVCT bands of species 3* - 5* decreased with rising electron withdrawing ability. However, the significant low intensity of the IVCT band of species 1* has been observed. Due to the poor solubility of iodoferrocene in PC, its IVCT band was not obtained.

Reference and Acknowledges
