

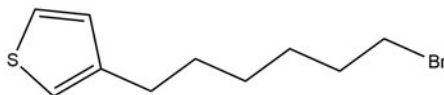
## 2 Experimental

### 2.1 Apparatus

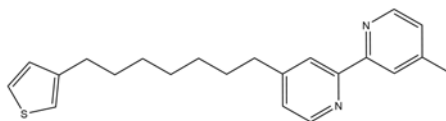
Electropolymerization, electrolysis as well as cyclic voltammetry were performed with the Jaislle Potentiostat-Galvanostat IMP 83PC-10. The headspace analysis was performed with the Thermo Scientific Trace GC Ultra Gas Injection Gas Chromatography while liquid gas chromatography with the Thermo Scientific Trace 1310 Liquid Injection Gas Chromatography. Ions analysis was performed with the Thermo Scientific Dionex Cap-IC. Thickness measurements were performed with DektakXT from Bruker.

### 2.2 Materials

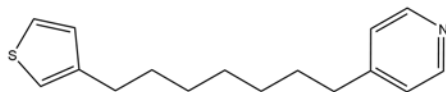
Pyridinium as well as Re-complexed bipyridines have been reported to work as homogeneous catalyst for CO<sub>2</sub> reduction [34, 40]. As heterogeneous catalysts can be reused easily our goal was to immobilize those materials on a Pt-electrode. The idea is to functionalize and electropolymerize thiophene to get an heterogeneous catalyst. In this thesis the synthesis of 3-(6-bromohexyl)thiophene (9) and 4-Methyl-4'-(3-thienylheptyl)-2,2'-bipyridine (10) is described. Compound 1 is used as precursor for the synthesis of 4-(3-thienylheptyl)pyridine (11) and compound 2 is used as precursor for the synthesis of [Re(4-Methyl-4'-(7-(3-thienyl)heptyl)-2,2'-bipyridinyl)(CO)<sub>3</sub>Cl] (12). The pyridine-functionalized and Re-complexed-functionalized thiophenes are electropolymerized, characterized and tested for CO<sub>2</sub> reduction.



**Figure 9:** chemical structure of 3-(6-Bromohexyl)thiophene:  
**compound 1**



**Figure 10:** chemical structure of 4-Methyl-4'-(3-thienylheptyl)-2,2'-bipyridine: **compound 2**



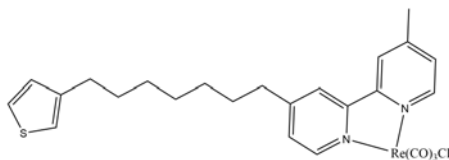
**Figure 11:** chemical structure of 4-(3-Thienylheptyl)-pyridine: **compound 3**

## 2.3 Setup for Electropolymerization

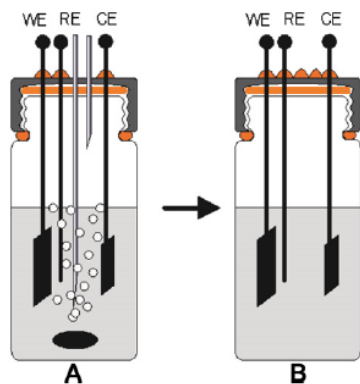
The polymerization is done in a three-electrode system in a one-compartment cell, which is shown in Figure 13. The working electrode and the counter electrode are Pt-plates. An Ag/AgCl-wire is used as quasi-reference electrode. In order to see if the film is working for CO<sub>2</sub>-reduction several cyclic voltammetry measurements are performed in an one-compartment cell using the polymer covered Pt-plate as working electrode, a Pt-plate as counter electrode and an Ag/AgCl-wire as a quasi-reference electrode. If the film does not cover the entire Pt-plate it is important that only the film dips to the solution, so one can be sure that the characteristics of the polymer are tested.

## 2.4 Setup for Electrolysis

For electrolysis a three-electrode system in a two-compartment H-cell is used, which is shown in Figure 14, is used. On one side of the cell the WE (Pt-plate with polymeric film, where only the film dips in to the solution) and an Ag/AgCl-wire as RE are fixed. On the other side of the cell the CE (Pt-plate), which faces the WE, is fixed. It is important that the system is sealed during the experiment.



**Figure 12:** chemical structure of [4-Methyl-4'-(3-thienylheptyl)-2,2'-bipyridinyl]Re(CO)<sub>3</sub>Cl]: **compound 4**



**Figure 13:** One-compartment cell for purging with N<sub>2</sub> (A) and during electropolymerization a closed system (B). Cells contain a working electrode (WE), a reference electrode (RE) and a counter electrode (CE) [39].

## 2.5 Calculation of the halfway-potential

For all the experiments a Ag/AgCl-quasi reference electrode is used. In order to determine the correction value for NHE a scan of Ferrocene needs to be performed. The setup, which is used, is equal to the setup used for the standard potential of the quasi reference electrode a CV using the Fc/Fc<sup>+</sup> couple is recorded. 0.1 M TBAPF<sub>6</sub> in acetonitrile is used as electrolyte and some crystals of Ferrocene are added. The scan range is from 0 mV to 900 mV and back to 0 mV. The halfway-potential is defined as

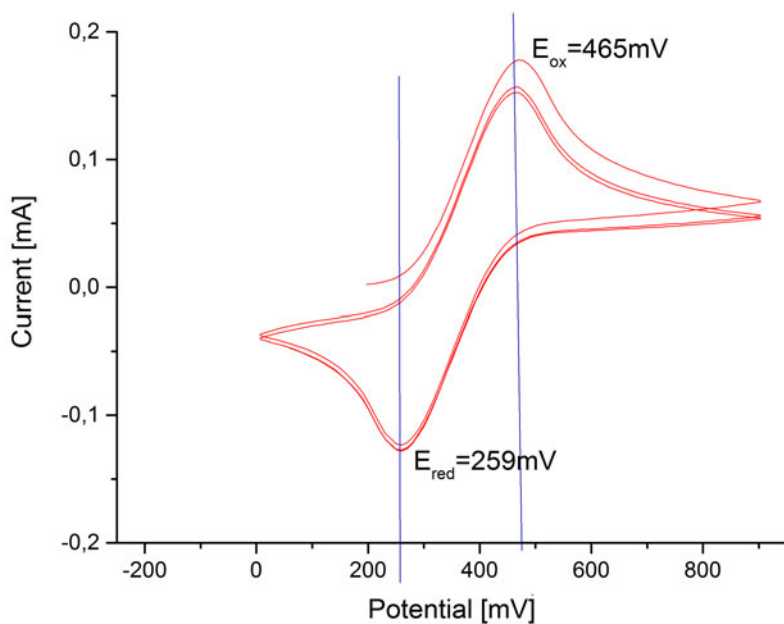
$$E_{1/2} = \frac{E_{red} + E_{ox}}{2}. \quad (2)$$



**Figure 14:** H-cell for electrolysis. The cell contains a WE (Pt-plate with polymeric film) and a Ag/AgCl-quasi RE on the one side of the cell and on the other side a CE (Pt-plate).

The voltammogram of Ferrocene is shown in Figure 15. According to Equation 2 the halfway potential of Ferrocene is 362 mV. The halfway potential of Ferrocene vs NHE is reported in the literature with 640 mV [41]. This means that the plots, where this Ag/AgCl-quasi RE is used, need to be shifted according to equation 3 in order to have the potential vs. NHE.

$$\Delta E = 640mV - 362mV = 278mV \quad (3)$$



**Figure 15:** Cyclic voltammogram measured of Ferrocene with a scanrate of  $10 \text{ mVs}^{-1}$  in  $0.1 \text{ M TBAPF}_6$  in acetonitrile.

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CO<sub>2</sub>-Reduction

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2015, XVII, 60 p. 37 illus., Softcover

ISBN: 978-3-658-10357-6