

Figure 1: Temperature changes over the last century
(<http://www.epa.gov/climatechange/science/causes.html> (09.04.2014)).

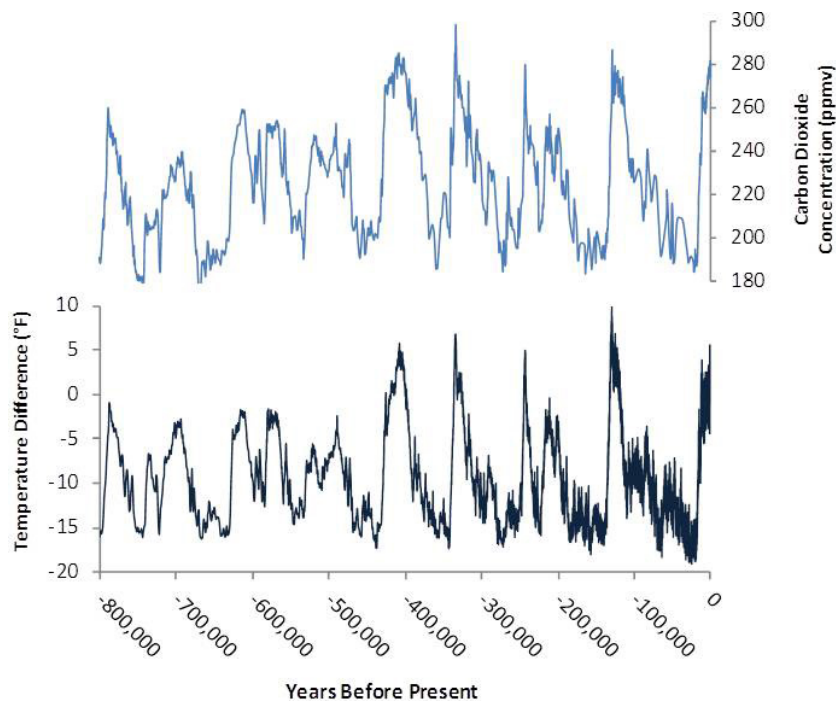


Figure 2: Correlation of Earth's surface temperature and the amount of carbon dioxide (<http://www.epa.gov/climatechange/science/causes.html> (09.04.2014)).

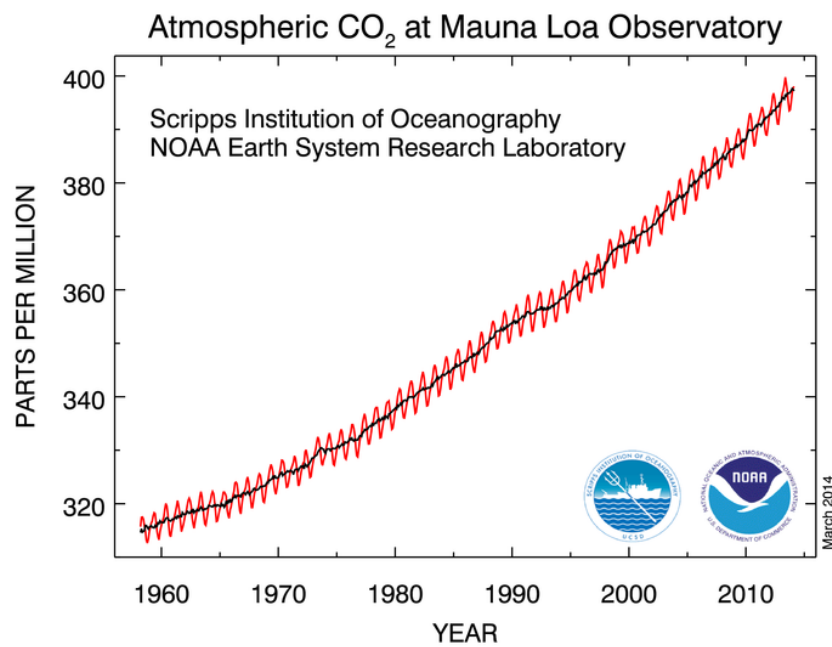


Figure 3: CO₂-measurement on Mauna Loa
(<http://www.esrl.noaa.gov/gmd/ccgg/trends/index.html> (09.04.2014)).

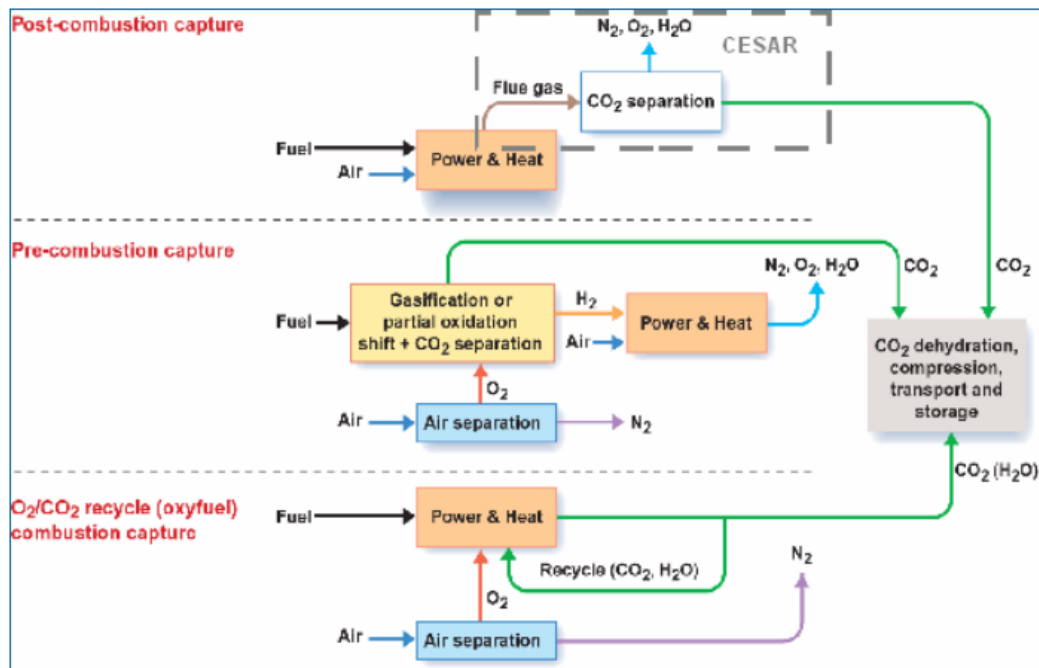


Figure 4: CO₂-separation principles
(http://www.co2cesar.eu/site/en/about_objectives.php (15.05.2014)).

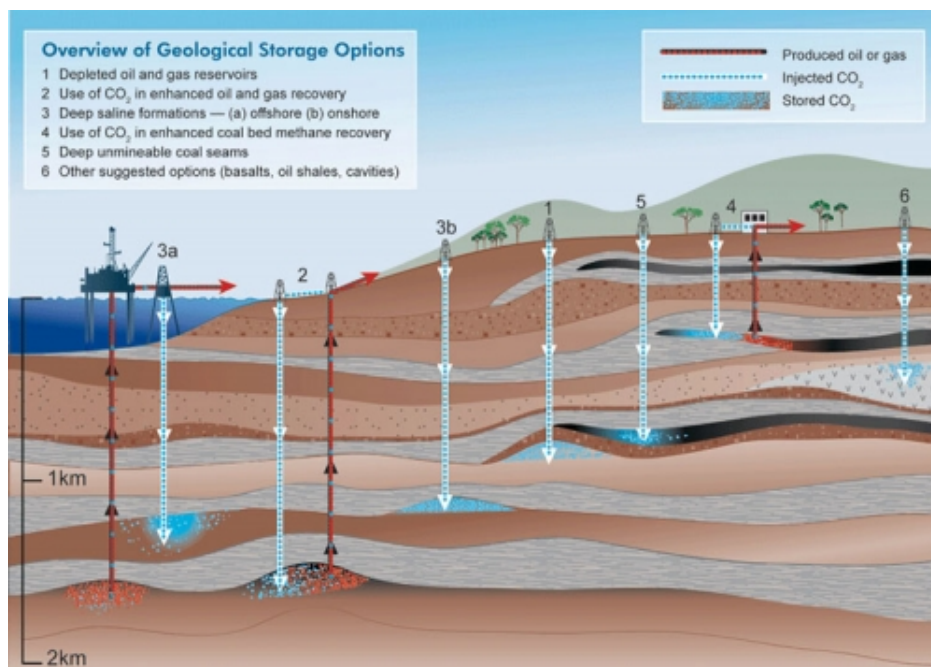


Figure 5: Geological storage options
(S. J. Friedmann. *Carbon Capture and Storage*.).

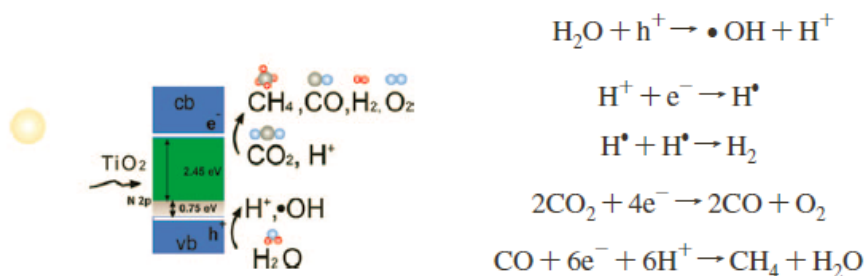


Figure 6: Sunlight-driven photocatalytic conversion of carbon dioxide to hydrocarbons

(O. K. Varghese, M. Paulose, T. J. LaTempa and C. A. Gries. *High-Rate Solar Photocatalytic Conversion of CO₂ and Water Vapor to Hydrocarbon Fuels.*).

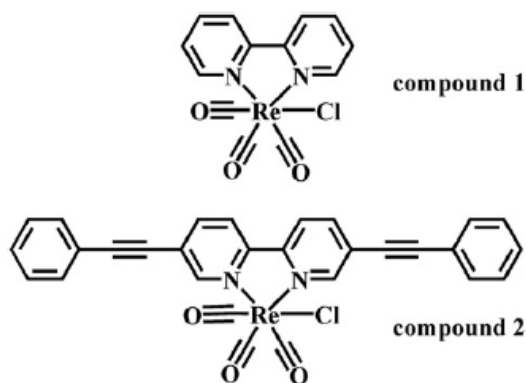


Figure 7: Chemical structure of (2,2'-bipyridyl)Re(CO)₃Cl (1) and (5,5'-bisphenylethynyl-2,2'-bipyridyl)Re(CO)₃Cl (2)

(E. Portenkirchner, K. Oppelt, Ch. Ulbricht, D. A. M. Egbe, H. Neugebauer, G. Knör and N. S. Sariciftci. *Electrocatalytic and photocatalytic reduction of carbon dioxide to carbon monoxide using the alkynyl-substituted rhenium(I) complex (5,5'-bisphenylethynyl-2,2'-bipyridyl)Re(CO)₃Cl.*).

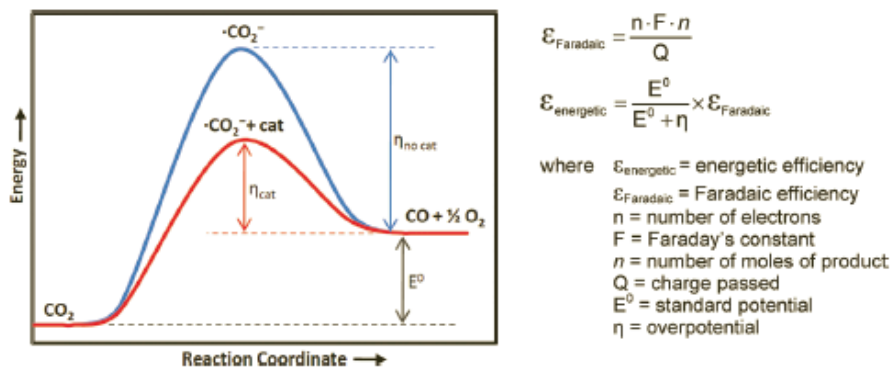


Figure 8: Qualitative reaction scheme for carbon dioxide conversion (D.T. Whipple and P.J.A. Kenis. *Prospects of CO₂ Utilization via Direct Heterogeneous Electrochemical Reduction.*).

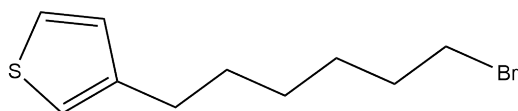


Figure 9: chemical structure of 3-(6-Bromohexyl)thiophene: **compound 1**

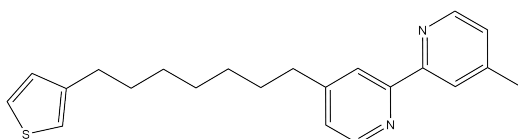


Figure 10: chemical structure of 4-Methyl-4'-(3-thienylheptyl)-2,2'-bipyridine: **compound 2**

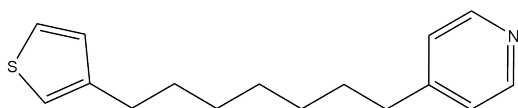


Figure 11: chemical structure of 4-(3-Thienylheptyl)-pyridine: **compound 3**

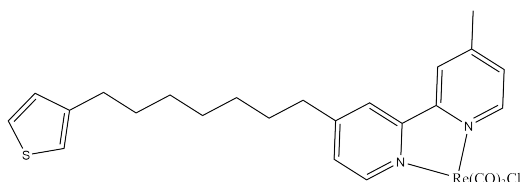


Figure 12: chemical structure of [4-Methyl-4'-(3-thienylheptyl)-2,2'-bipyridinyl]Re(CO)₃Cl: **compound 4**

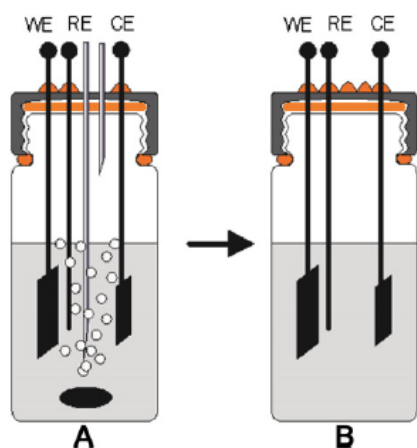


Figure 13: One-compartment cell for purging with N₂ (A) and during electropolymerization a closed system (B). Cells contain a working electrode (WE), a reference electrode (RE) and a counter electrode (CE)
(E. Portenkirchner, K. Oppelt, Ch. Ulbricht, D. A. M. Egbe, H. Neugebauer, G. Knör and N. S. Sariciftci. *Electrocatalytic and photocatalytic reduction of carbon dioxide to carbon monoxide using the alkynyl-substituted rhenium(I) complex (5,5'-bisphenylethynyl-2,2'-bipyridyl)Re(CO)₃Cl.*).



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).

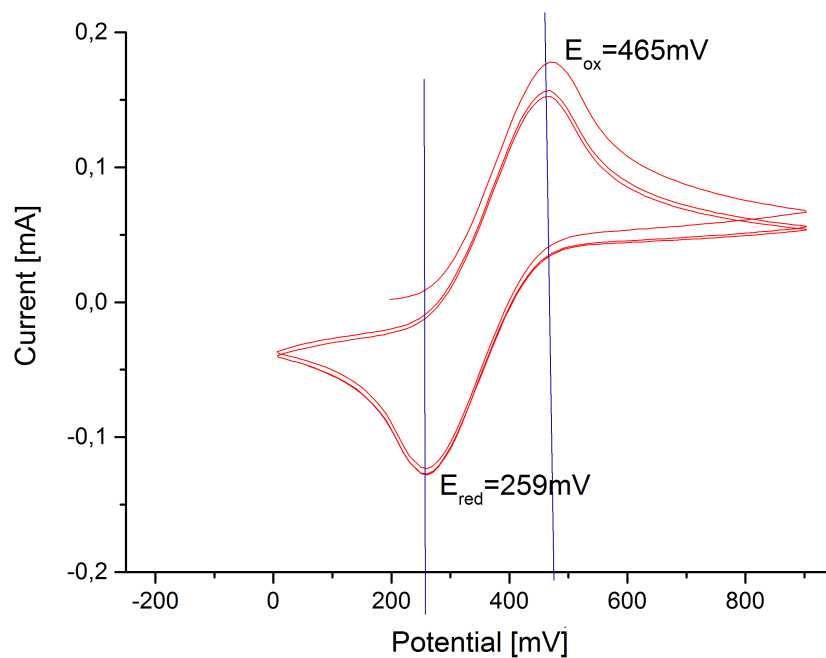


Figure 15: Cyclic voltammogram measured of Ferrocene with a scanrate of 10 mVs^{-1} in 0.1 M TBAPF_6 in acetonitrile.

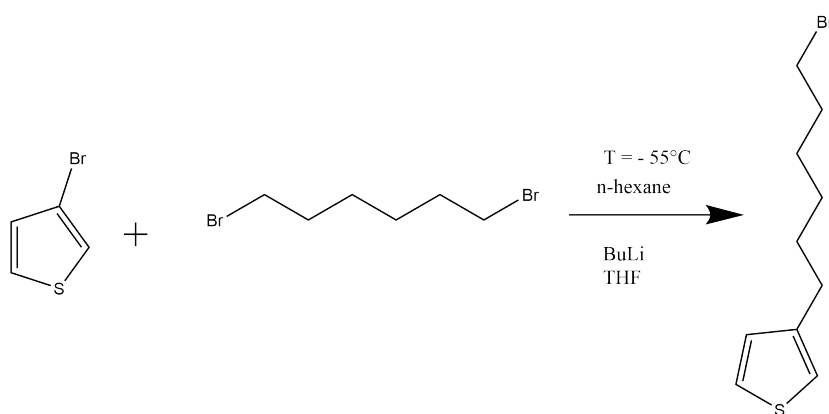


Figure 16: reaction scheme for synthesis of 3-(6-bromohexyl)thiophene

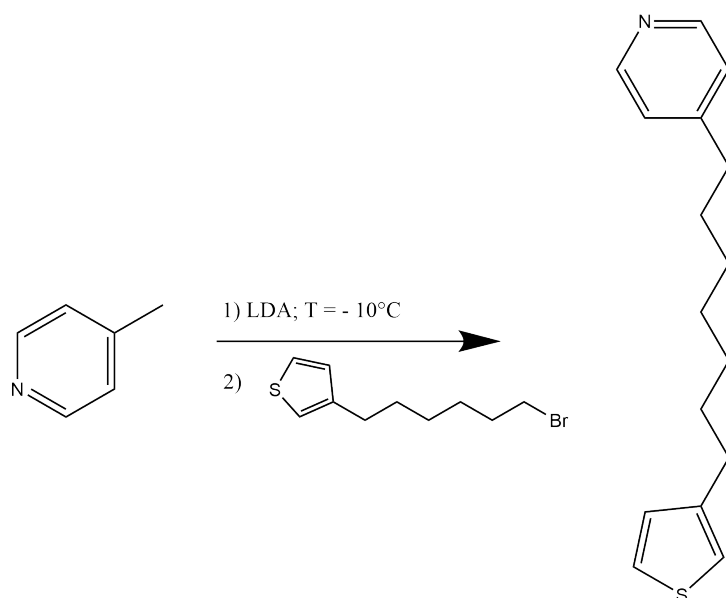


Figure 17: reaction scheme for synthesis of 4-(3-thienylheptyl)pyridine

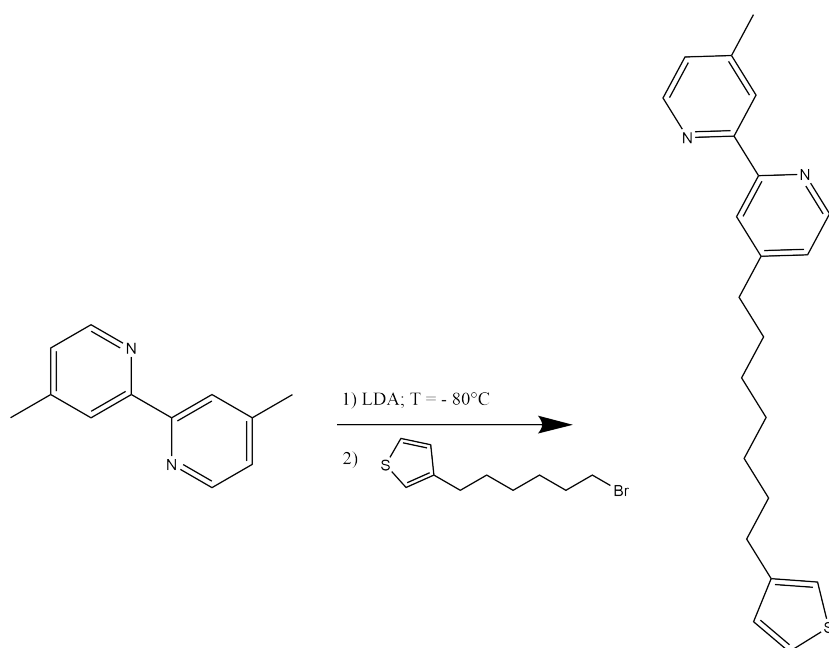


Figure 18: reaction scheme for synthesis of 4-methyl-4'-(3-thienylheptyl)-2,2'-bipyridine

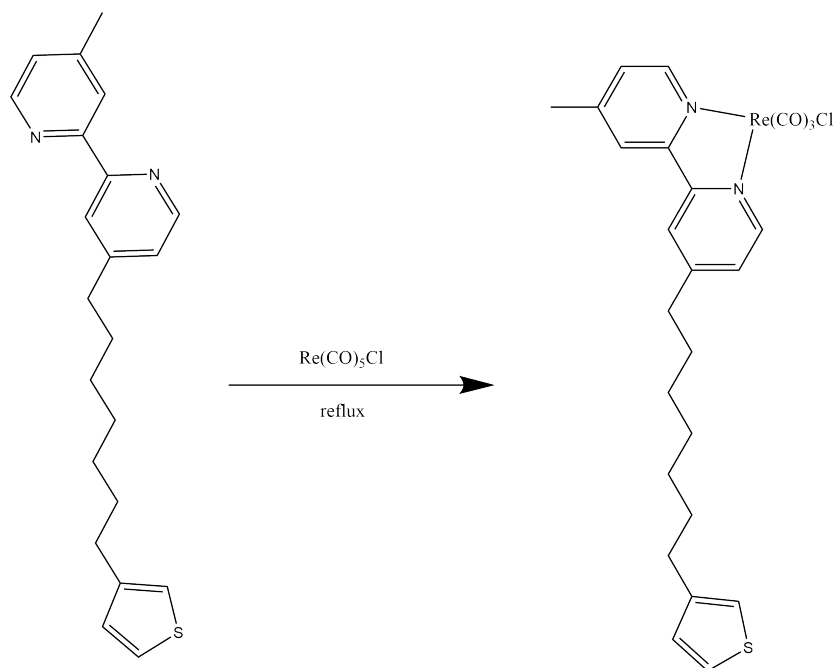


Figure 19: reaction scheme for synthesis of [4-methyl-4'-(3-thienylheptyl)-2,2'-bipyridine]Re(CO)₃Cl

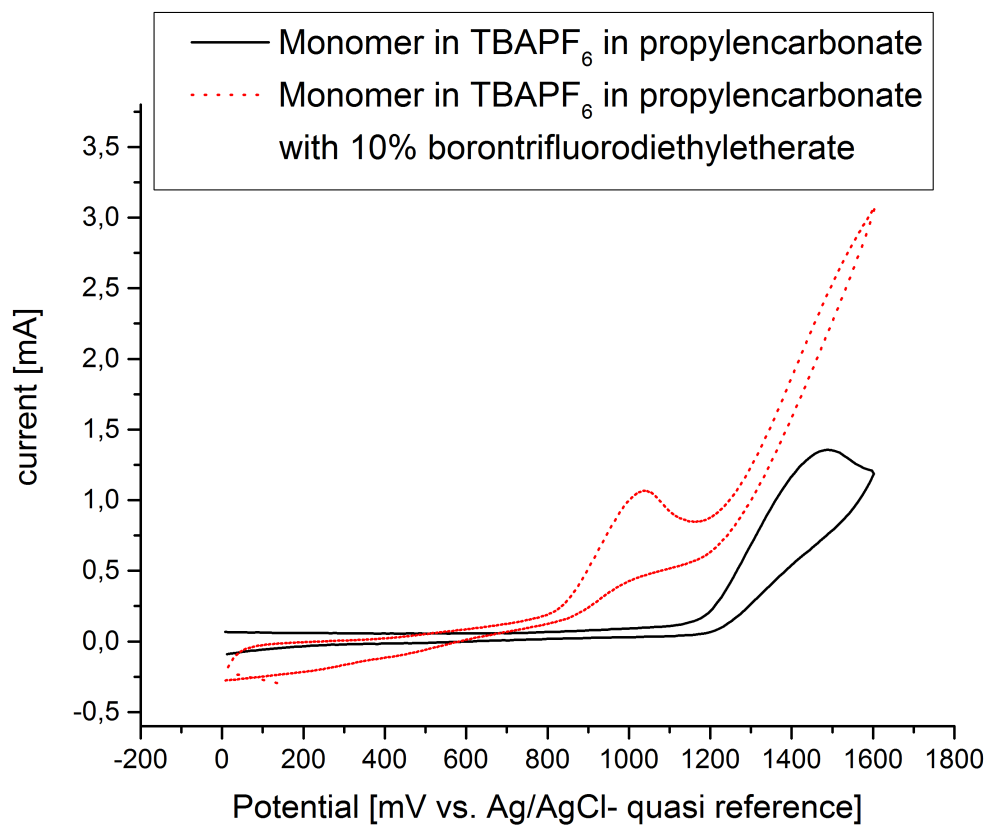


Figure 20: Scan from 0 mV to 1600 mV and back to 0 mV of [Re(4-Methyl-4'-(7-(3-thienyl)heptyl)-2,2'-bipyridinyl)(CO)₃Cl] monomer in 0.1 M TBAPF₆ in propylencarbonate and after adding 10 % of BFEE with a scanrate of 100 mVs⁻¹.

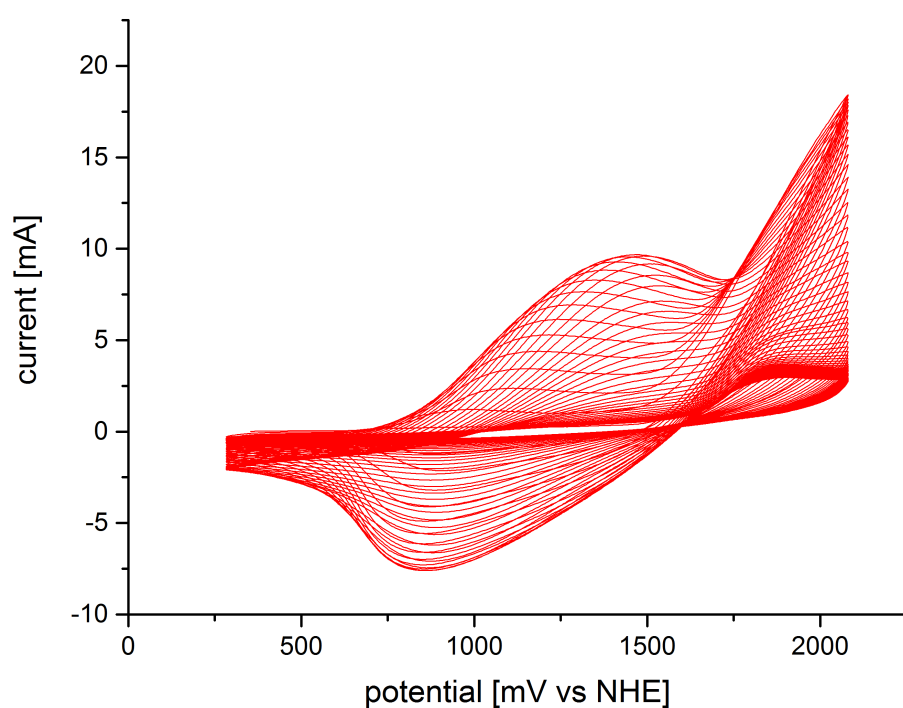


Figure 21: Potentiodynamic electropolymerization of 4-(3-Thienylheptyl)-pyridine. The polymerization is done in an one compartment-cell where a Pt-plate was used as working electrode. The counter electrode was also a Pt-plate and an Ag/AgCl-wire was used as quasi-reference electrode.

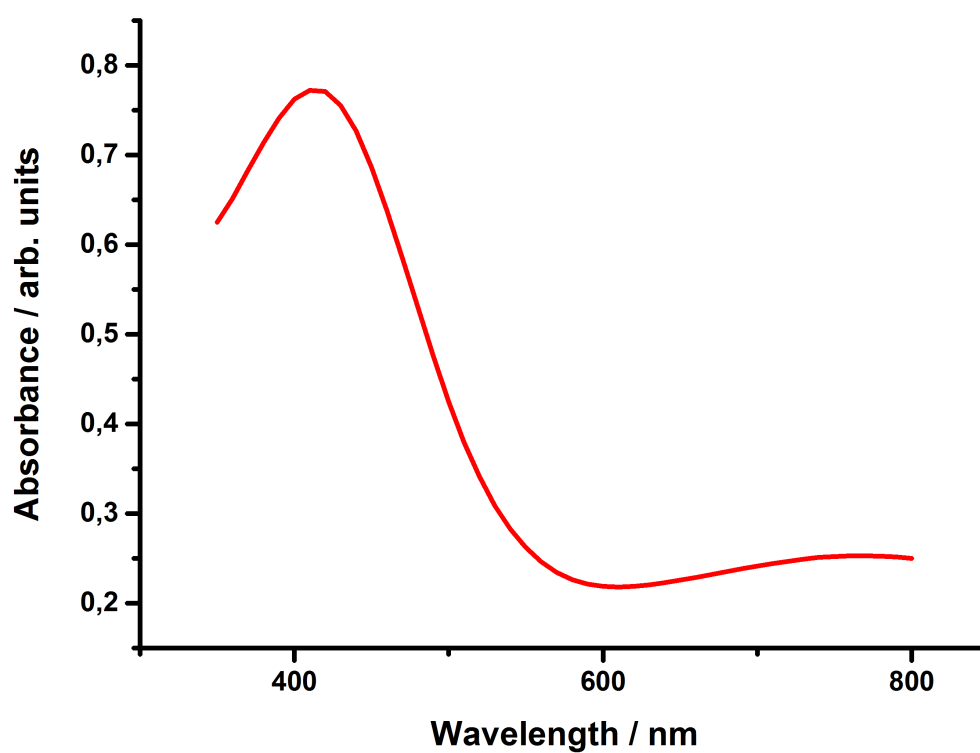


Figure 22: UV-vis measurement of pyridine functionalized poly- (thiophene) film on glass-ITO.

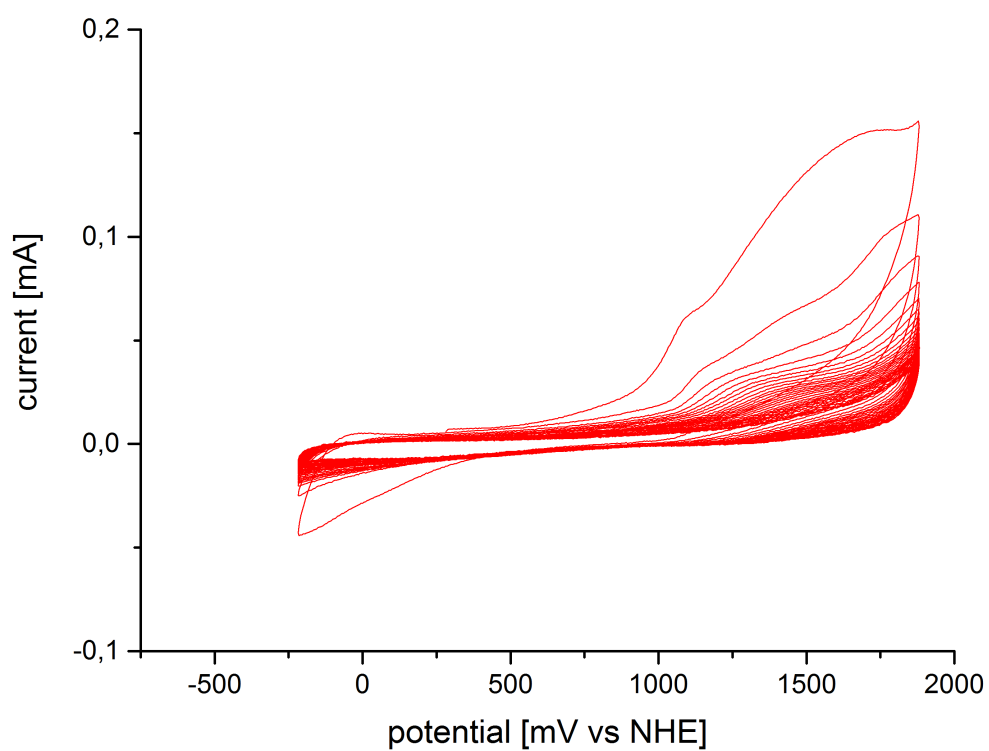


Figure 23: Potentiodynamic electropolymerization of 4-Methyl-4'-(7-(3-thienyl)heptyl)-2,2'-bipyridine with a scan rate of 50 mVs^{-1} in 0.1 M TBAPF₆ in propylen carbonate with 10% BFEE.



Figure 24: Complexation of poly-4-methyl-4'-(3-thienylheptyl)-2,2'-bipyridine film with $\text{Re}(\text{CO})_5\text{Cl}$ in hot toluene.

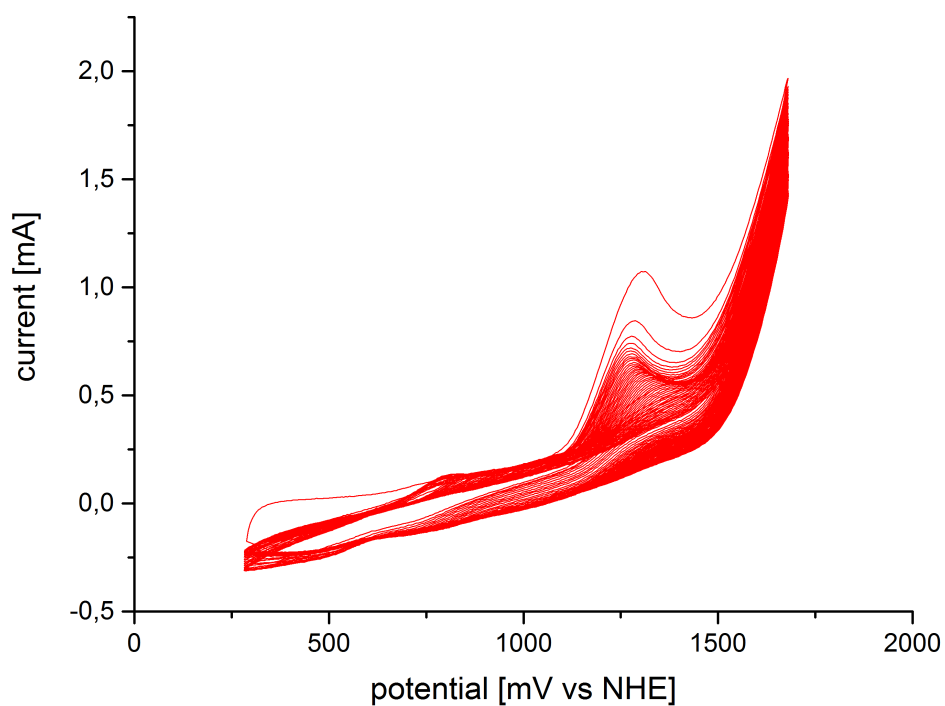


Figure 25: Potentiodynamic electropolymerization of $[\text{Re}(4\text{-Methyl-4'-(7-(3\text{-thienyl)heptyl)-2,2'-bipyridinyl})(\text{CO})_3\text{Cl}]$. The polymerization is done in an one compartment-cell where a Pt-plate was used as working electrode. The counter electrode was also a Pt-plate and an Ag/AgCl-wire was used as quasi-reference electrode.

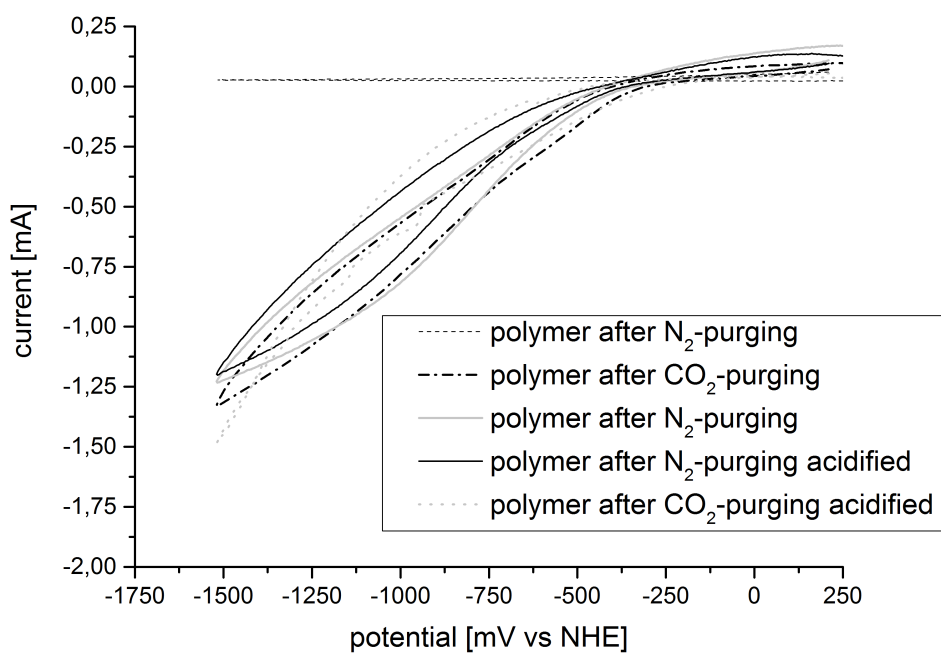


Figure 26: Cyclic voltammogram of polymeric-4-(3-Thienylheptyl)-pyridine-film measured with a scanrate of 50 mVs^{-1} . The polymerization is done in an one compartment-cell where a Pt-plate covert with the polymer was used as working electrode. The counter electrode was also a Pt-plate and an Ag/AgCl-wire was used as quasi-reference electrode. 0.1 M TBAPF_6 in acetonitrile is used as electrolyte.

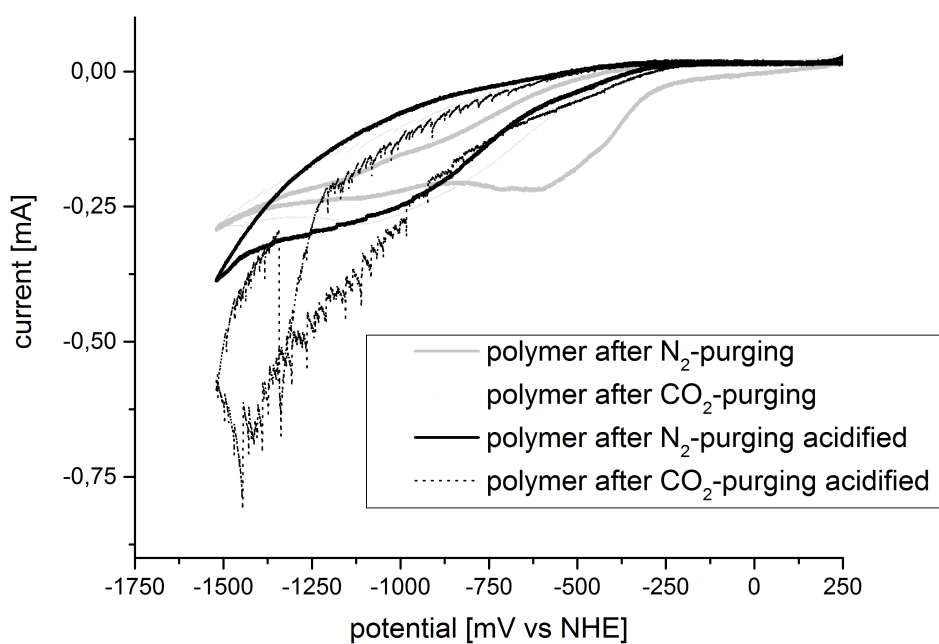


Figure 27: Cyclic voltammogram of polymeric-4-(3-Thienylheptyl)-pyridine-film measured with a scanrate of 1 mVs^{-1} . The polymerization is done in an one compartment-cell where a Pt-plate covert with the polymer was used as working electrode. The counter electrode was also a Pt-plate and an Ag/AgCl-wire was used as quasi-reference electrode. 0.1 M TBAPF_6 in acetonitrile is used as electrolyte.

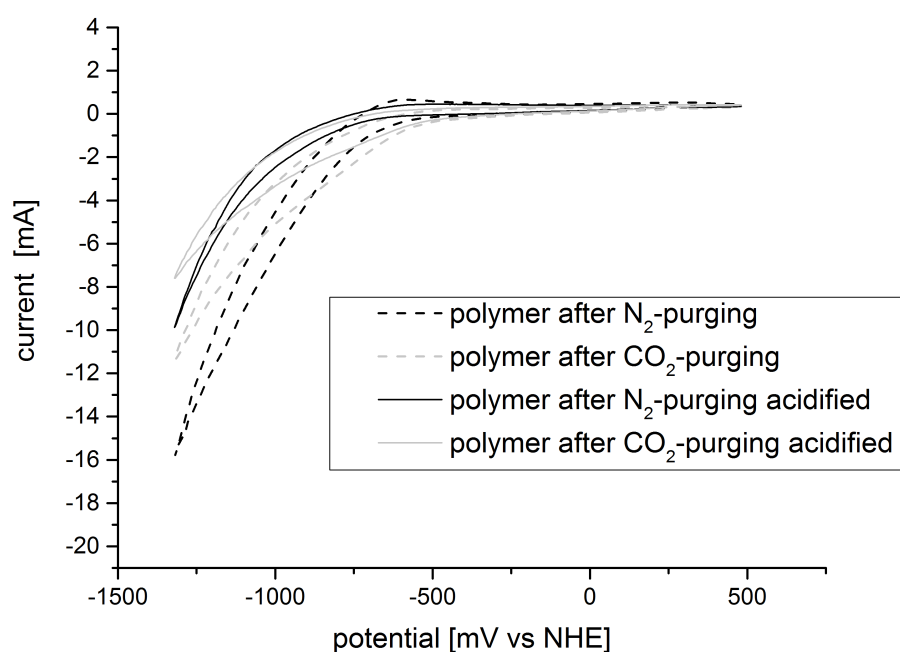


Figure 28: Cyclic voltammogram of polymeric-4-(3-Thienylheptyl)-pyridine-film measured with a scanrate of 50 mVs^{-1} . The polymerization is done in an one compartment-cell where a Pt-plate was used as working electrode. The counter electrode was also a Pt-plate and an Ag/AgCl-wire was used as quasi-reference electrode. 0.5 M KCl is used as electrolyte.

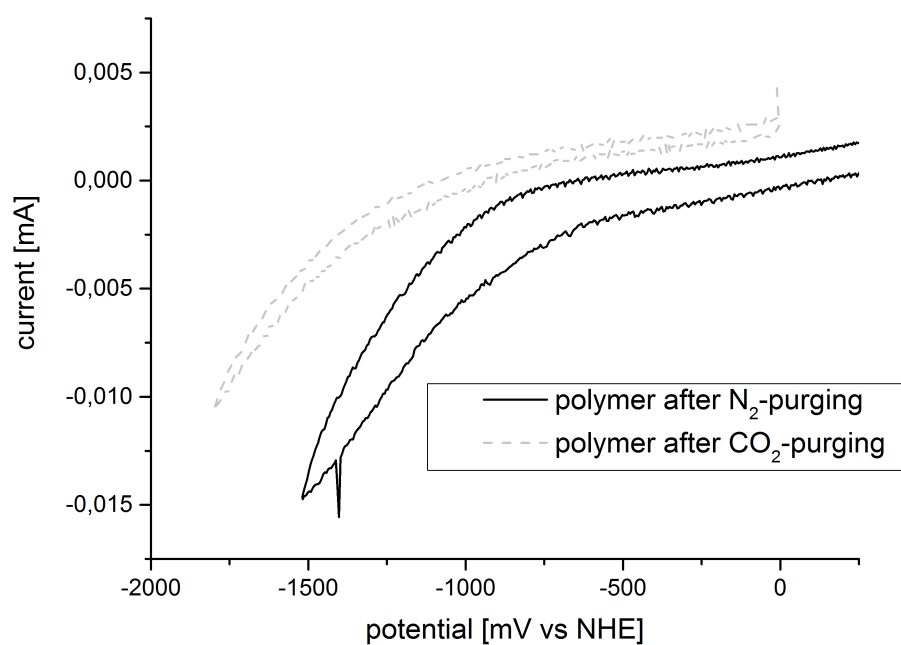


Figure 29: Cyclic voltammogram measured of the Re-complexed polymeric film with a scanrate of 10 mVs^{-1} in 0.1 M TBAPF_6 in propylen carbonate

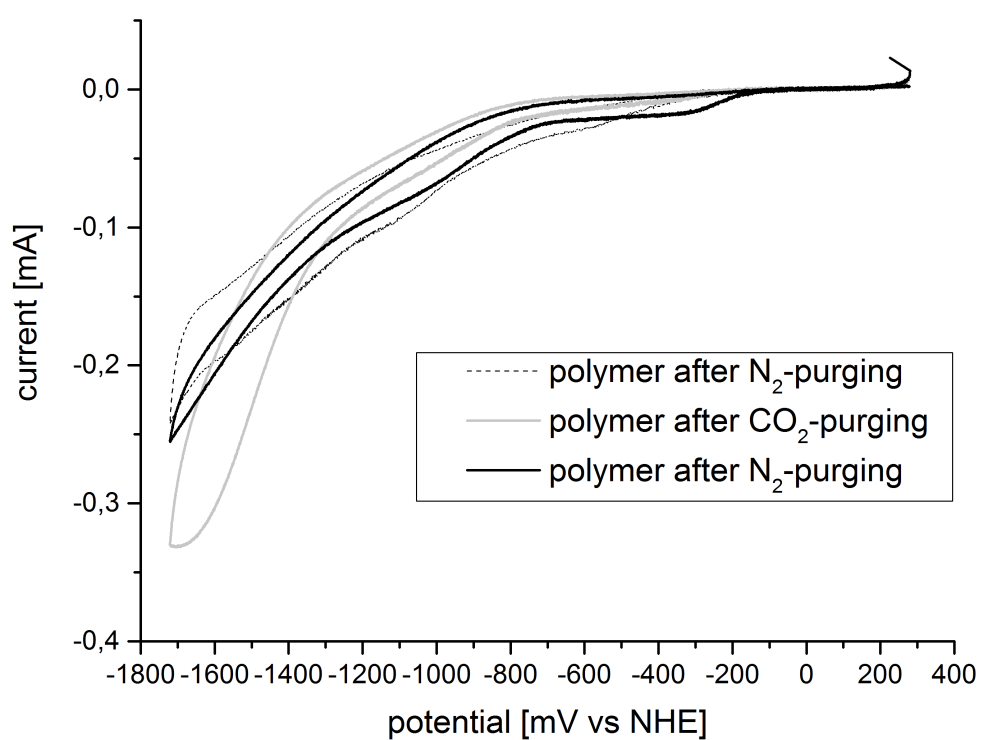


Figure 31: Characterization of [Re(4-Methyl-4'-(7-(3-thienyl)heptyl)-2,2'-bipyridinyl)(CO)₃Cl] film in 0.1 M TBAPF₆ in acetonitrile.

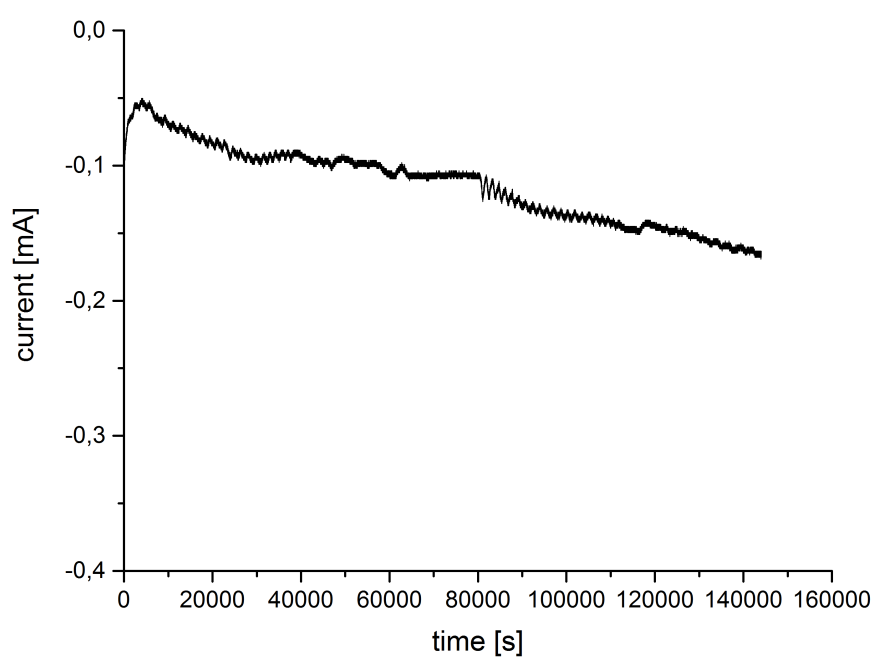


Figure 32: 40 hour electrolysis of pyridine functionalized poly(thiophene) in 0.1 M TBAPF₆ in acidified acetonitrile. Holdvalue at a potential of -1200 mV.



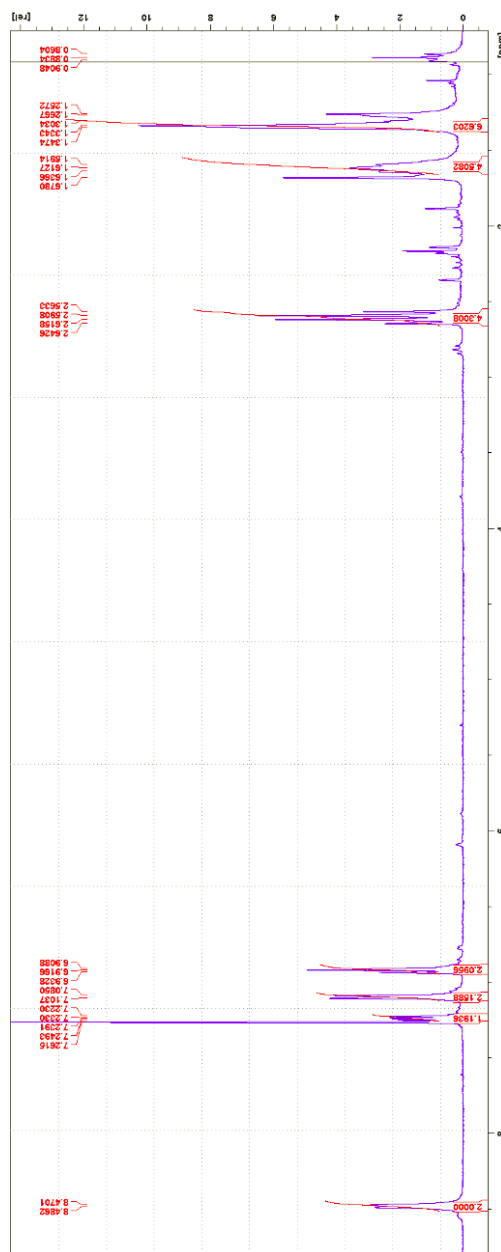
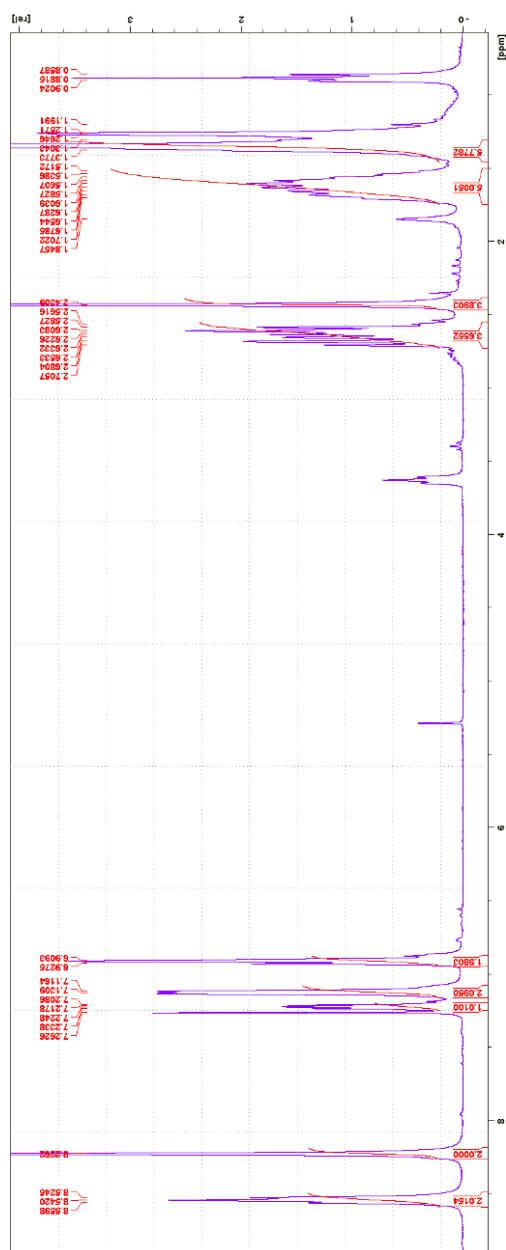


Figure 35: ¹H-NMR of 4-(3-thienyl)heptylpyridine in CDCl₃



Pyridine-functionalized Polymeric Catalysts for
CO₂-Reduction

Weichselbaumer, M.

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