

Catalysis

Photoelectrochemical Reduction of CO₂ Using Third-Generation Conjugated PolymersDogukan H. Apaydin,^{*[a]} Elisa Tordin,^[a] Engelbert Portenkirchner,^[a] Gottfried Aufischer,^[a] Stefanie Schlager,^[a] Melanie Weichselbaumer,^[a] Kerstin Oppelt,^[b] and Niyazi Serdar Sariciftci^[a]

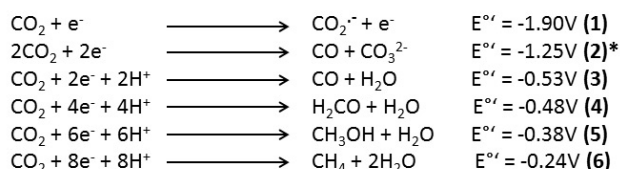
Third-generation polythiophenes, bearing Rhenium carbonyl complexes and pyridinium as pendant active sites were used to drive the photoelectrochemical reduction of CO₂. Cyclic voltammetry and controlled potential electrolysis experiments were performed in CO₂-saturated acetonitrile, acetonitrile-water and aqueous solutions under illumination as well as in dark. The formation of CO was confirmed with IR spectroscopy and quantified with gas chromatography in the case of *poly*-[Re-(4-methyl-

4'-(7-(thiophen-3-yl)heptyl)-2,2'-bipyridyl)tricarbonylchloride] giving a max. Faradaic efficiency of 2.5% and a Turnover number of ~20. In the case of *poly*-[4-(7-(thiophen-3-yl)heptyl)pyridine] which was supposed to catalyse reduction reaction of CO₂ to MeOH, no products were observed. Although the initial efficiencies are not high due to the surface limited processes, this immobilization of such catalysts on the photoelectrode might be industrially attractive.

Introduction

The direct reduction of CO₂ to CO₂ radical anion usually requires a high negative potential of nearly -1.90 V vs. normal hydrogen electrode (NHE) for a one-electron reduction.^[1] However, the actual redox potential is much higher than this Nernst potential owing to barrier-induced overpotentials. Such a problem can be overcome by introducing different reaction pathways that involve (multi)electron processes (Equations 1-6) mediated by a suitable catalyst as electron shuttle to obtain products like carbon monoxide or methanol.^[2-4]

In this context, Rhenium complexes with bipyridine (bipy) ligands demonstrate excellent properties in terms of activities and lifetimes for the selective homogeneous CO₂ reduction to CO.^[7] In particular, in 1984 Jean Marie Lehn *et al.* reported the complex [Re(2,2'-bipyridyl)(CO)₃Cl], which was found to show high Faradaic efficiencies and no significant decrease in performance over several hours.^[8]



Equations 1-6. Thermodynamic formal potentials for various CO₂ reduction products (pH 7 in aqueous solutions versus NHE). *Thermodynamic reduction potential for CO₂ in acetonitrile^[5,6]

Furthermore, Ley and Schanze have studied the excited-state properties of several different Re-bipyridine complexes in great detail.^[9] Later on, Kubiak *et al.* reported a systematic study of the catalytic activity of a series of [Re(bipyridyl)(CO)₃Cl] complexes with varying degrees of electron donating/withdrawing substituents in the 4, 4' positions of the bipyridine chelating ligand.^[10] The same group also reported the selective photoreduction of CO₂ to CO on a planar p-type H-Si photocathode in presence of the homogeneous rhenium bipyridine electrocatalyst.^[11] The photocatalytic reaction occurs at relatively low photovoltage and good Faradaic efficiency. Moreover, our group recently reported the homogenous electro- and photocatalytic CO₂ reduction promoted by the alkynyl-substituted Re complex [Re(5,5'-bisphenylethynyl-2,2'-bipyridyl)(CO)₃Cl] as well as its synthesis, structure, photophysics, and spectroscopic characterization.^[12] The latter compound showed a lower reduction potential and higher rate constant for the reduction of CO₂ to CO than the Re-based catalysts reported previously.

On the quest to a multi-electron-reduction pathway, in 1994 Bocarsly *et al.*^[13] first reported the use of pyridinium ions as homogeneous catalyst for the electrochemical reduction of CO₂ to the 6e⁻ reduction product of methanol. At hydrogenated Pd electrodes, faradaic efficiencies for the reduction of CO₂ to

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methanol of ~30% were observed at overpotentials of only ~200 mV. Detailed kinetic, mechanistic and structural studies indicate that the complete reduction of CO₂ to the 6e⁻ reduced product of methanol goes sequentially through the 2e⁻ and 4e⁻ reduced intermediates formic acid and formaldehyde, respectively. It is important to point out that, while the proposed mechanism is best described as a globally homogeneous process, they did not elucidate the specifics of the surface interactions nor the reason why the reaction seems to occur only in presence of Pt or Pd electrodes.^[14,15] The same group exported the pyridinium-catalysed CO₂ reduction chemistry to a p-GaP photoelectrochemical system which yielded to nearly 100% faradaic efficiency for methanol by applying potentials 300 mV lower than the thermodynamic potential of -0.52 V vs SCE at pH of 5.2^[16]. No other products were detected. This is the first reported system capable of reducing CO₂ to methanol using energy from light only. This result was very promising and fueled a lot of discussion in the field^[17-21] but the catalytic system is still homogeneous and therefore limited with respect to possible application on the industrial level.

The molecules described above have a trait in common: they are all homogeneous catalytic systems. Although homogeneous catalytic systems are (most of the time) easier to characterize and mechanistically better understood than many heterogeneous ones, their application can have several disadvantages. Large amounts of expensive catalyst are necessary for efficient CO₂ reduction (~10mg Lehn catalyst is required for 1mL CO produced)^[8] and only the catalyst molecules which are in the vicinity of the electrode surface will be active while the rest is serving to no purpose. Furthermore, homogeneous catalysts may sometimes face solution deactivation pathways, such as the formation of dimers observed in certain rhenium bipyridine complexes in non-aqueous solution.^[22,23] One way to overcome these problems is to immobilize the catalyst on an electrode and thereby switch from homogeneous to heterogeneous catalysis. The most frequently reported ways to immobilize Re catalysts onto solid electrodes were either the insertion of the molecule into a polymer matrix^[6,24,25] or the chemical modification of the ligand with a functional group that allowed polymerization to form a redox polymer.^[26-29]

The second approach was followed by Portenkirchner et al. and they reported the electropolymerisation of [Re(5,5'-bisphenylethynyl-2,2'-bipyridyl)(CO)₃Cl] onto a platinum electrode. The polymerised film was tested for the conversion of CO₂ to CO and 33% of Faradaic efficiency at -1150mV vs NHE was observed.^[30]

A different approach concerning the attachment of functional groups to the backbone of a conducting polymer was suggested by Sariciftci *et al.* in 1992, resulting in what is called the "third generation" of conjugated polymers.^[31] With this approach it is anticipated to achieve sophisticated molecular structures with specific physical and/or chemical properties for advanced application possibilities in redox catalysis (Figure 1).

Following this idea, we report in this paper the preparation of polythiophene polymers functionalised with [fac-(2,2'-bipyridyl)Re(CO)₃Cl] and pyridine units leading polymers (Figure 2); P[3HRe(bpy)(CO)₃Cl-Th] and P[3HPyr-Th] and their full electro-

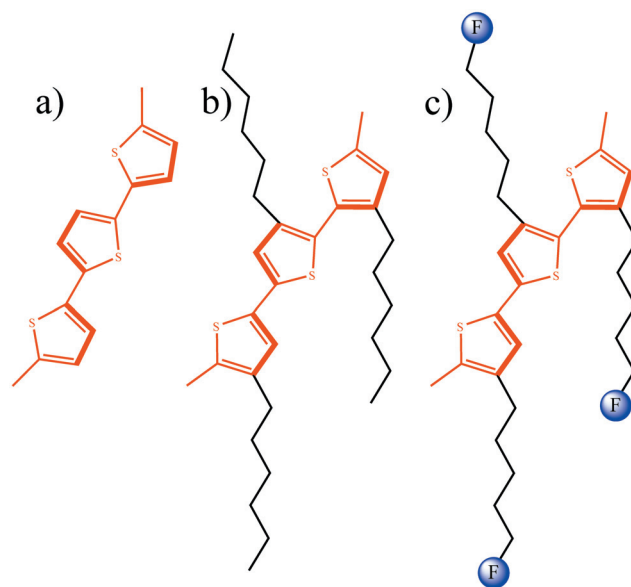


Figure 1. Three generations of conjugated polymers; a) Polymers with good conductivity but low processability, b) Polymers with alkyl chains allowing solubility hence processability, c) Polymers with improved and/or new physical/chemical and catalytic properties.^[31]

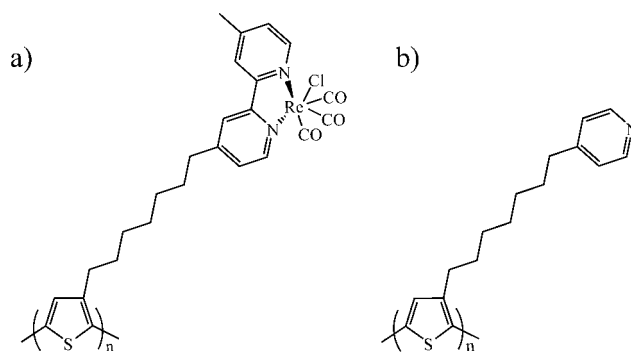


Figure 2. Chemical structures of a) P[3HRe(bpy)(CO)₃Cl-Th] and b) P[3HPyr-Th].

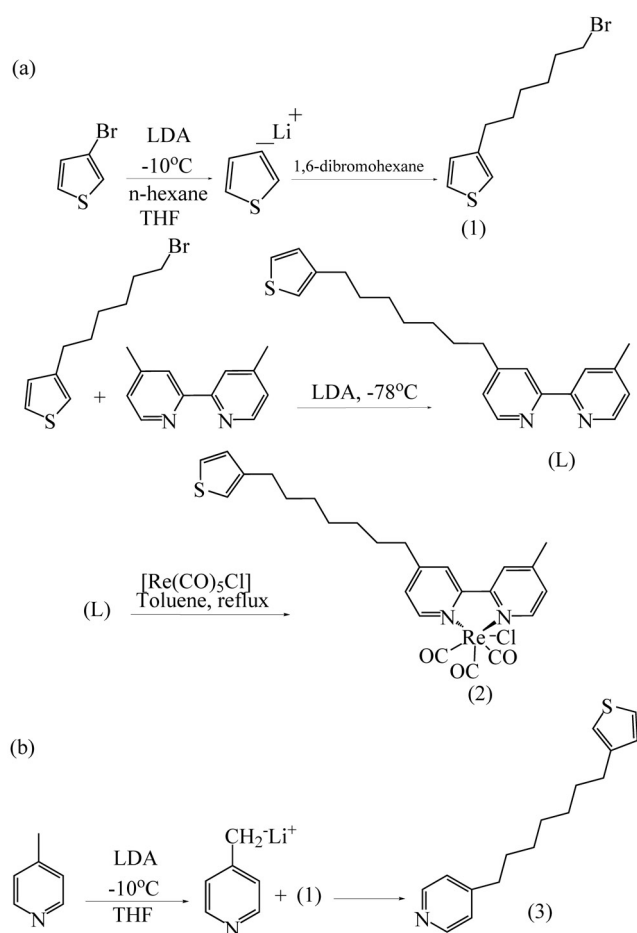
chemical characterization together with the study of their catalytic activity toward photoelectrochemical CO₂ reduction. Polythiophene was chosen as polymeric backbone for its relative stability to both oxygen and moisture and its versatility in photo/electrochemistry. Polythiophene, being a p-type organic semiconductor is not suitable for supporting electrons, hence n-type processes like CO₂ reduction. However, when illuminated polythiophene can transfer an electron to the catalyst material from its LUMO level while the hole in the HOMO level can recombine with an electron coming from the electrode to complete the circuit^[32]. With these prerequisites fulfilled polythiophene can act as both a supporting backbone for the catalyst and facilitate n-type charge transport through itself to the catalyst material to reduce CO₂ to further products. We would like to point out that the idea in this work differs from the previous study^[30] with an ability of to be applied as a general

method. In the study of Portenkirchner *et al.* the idea was focused on incorporating the Re-complex in the backbone via chemical modification. With the approach we can modify the side chain easily while keeping a relatively well studied polymer backbone. Synthetic methods described in this study can be adapted to many catalyst molecules hence opening a new route to heterogeneous catalysis using the known homogeneous catalysts. Plus we also employ the photocurrent effect coming from backbone itself leading to a combined result of photoelectrochemical catalysis.

Results and Discussion

Synthesis

A schematic representation of the synthetic procedure followed for (1), (2) and (3) is reported in Scheme 1. The synthesis



Scheme 1. Synthetic route for (a) $[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ and (b) $[3\text{HPyr-Th}]$ ^[33]

of the precursor 1 proceeded via formation of the 3-thienyl carbanion followed by coupling with 1,6-dibromohexane.^[33] This last one has to be freshly distilled prior to use and the stoichiometric excess vs 3-bromothiophene is necessary to avoid the formation of 1,6-dithienylhexane. We found only one bro-

mine atom will be substituted by the thienyl unit if the 1,6-dibromo is in strong excess when compared to the 3-thienyl carbanion.

L is synthesized by deprotonation of the methyl groups of 4,4'-dimethyl-2,2'-bipyridyl by a strong base, in this case lithium diisopropylamide (LDA), followed by coupling with 3-(6-bromohexyl)thiophene (1). Following this approach, a mixture of mono- (L) and bi-substituted ligand has always been obtained and the ratio between those products has been controlled by the stoichiometry between the starting bipyridyl material and the LDA. It is important to point out that the polarity of the functionalized ligands is not that different from the one of the starting material 4,4'-dimethyl-2,2'-bipyridyl and it is impossible to separate one from the others by column chromatography. It is however, easily possible to separate the species after complexation with the rhenium precursor. For the synthesis of L, it is crucial to keep the 4,4'-dimethyl-2,2'-bipyridyl in excess compared to the lithium diisopropylamide (LDA) during the deprotonation step. This can be achieved by making sure that the starting material is fully solubilized in THF even at low temperature and by adding the LDA dropwise and slowly. In such a way, the strong base, for statistical reasons, is most likely to deprotonate only one of the methyl groups of the starting material. The 3-(6-bromohexyl)thiophene is, then, added in stoichiometric amount. The deprotonation/coupling reaction doesn't proceed quantitatively so it is necessary, after workup, to remove the excess of 3-(6-bromohexyl)thiophene by filtration on neutral alumina using a mixture of CHCl_3 and n-hexane (1:1 v/v) as eluent. The synthesis of the complexes is performed by adaptation of the recipes reported by Kubiak *et al.* for differently substituted bipyridyl ligands^[10]. A toluene solution containing a mixture of the thiophene substituted bipyridine ligands and an equimolar amount of the rhenium precursor $[\text{Re}(\text{CO})_5\text{Cl}]$ (equimolar to the amount of starting bipyridine ligand) is refluxed for 1 hour and the products 2 are isolated after column chromatography on silica. The overall yields of these reactions are quite low (6% for 2 calculated vs the amount of 4,4'-dimethyl-2,2'-bipyridyl) and the least efficient synthesis step is by far the preparation of the ligand L since the complexation reaction occurs quantitatively. The synthesis of (3) consists of the deprotonation of 4-picoline with Lithium diisopropylamide followed by nucleophilic substitution of the bromine atom of (1). The product was isolated as pure yellow-brown oil after column chromatography in neutral alumina.

Electropolymerization of (2) and (3)

Monomer $[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ was polymerized in a one-compartment cell containing Boron trifluoride diethyl etherate (BFEE) as the supporting electrolyte and the solvent with a three-electrode system. A simple Pt plate was used as working electrode and thus as substrate for the polymer film. A silver wire coated with silver chloride which was calibrated against Fc/Fc^+ served as a quasi-reference electrode where another Pt plate was used as counter electrode. Polymerization was carried out under N_2 atmosphere by cycling the potential between 300mV and 1700mV vs. NHE. Over the course of polymerization

the peak of monomer oxidation which is around 1200mV vs. NHE, decreased while the broad peak between 600mV and 900mV increased suggesting the polymer growth (Figure 3)

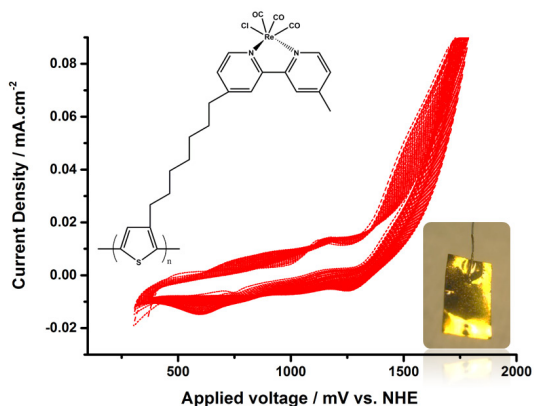


Figure 3. Cyclic voltammogram depicting the potentiodynamic polymerization of $[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$. Inset: Photo of a very thick film of the polymer in shiny gold color.

leading to $\text{P}[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$. At the end of the polymerization the surface of the Pt was fully covered with a thin layer of pale yellow polymer film. For the purpose of visualization, Figure 3 contains a photo of a very thick film of the polymer in shiny gold color as an inset figure. However, such thick films did not show any catalytic activity. For this reason thinner films represented with their CV scans in Figure 3 were used throughout all experiments.

The changes between the first and 45th cycle of polymerization of $\text{P}[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ were not as big as for example compared to the changes in the case of $\text{P}[3\text{HPyr-Th}]$ because the concentration of monomer in $\text{P}[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ was an order of magnitude lower. This explains the atypical CV scan compared to an expected one from electropolymerization of thiophene.

In the case of $[3\text{HPyr-Th}]$ the electrolyte solution consisted of 10% (by volume) BFEe in 0.1M tetrabutylammonium hexafluorophosphate (TBAPF_6) in acetonitrile. Figure 4 shows the cyclic voltammogram for the polymerization of the monomer.

Photoelectrochemical Reduction of CO_2

$\text{P}[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ was immersed in 0.1M TBAPF_6 solution in acetonitrile in an H-Cell together with an Ag/AgCl quasi reference electrode in the cathode chamber. Pt plate was used as counter electrode in the anode chamber. Both chambers were closed using a cap with a septum in the middle. The electrochemical setup was sealed and then both chambers were purged first with N_2 with a flow rate of 0.2L/min for 45min. For the evaluation of photoactivity of the electrode cyclic voltammograms were measured under dark and light conditions in N_2 atmosphere (Figure 5). The shift in the potential of both peaks

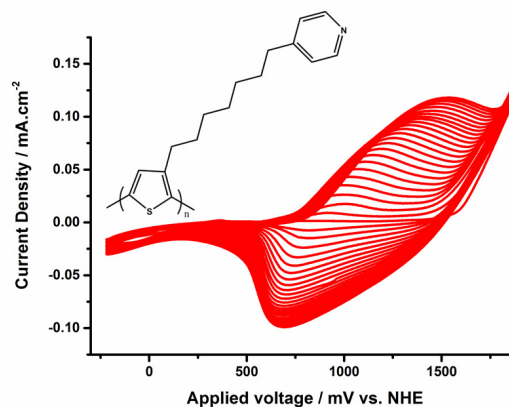


Figure 4. Cyclic voltammogram for the polymerization of $[3\text{HPyr-Th}]$.

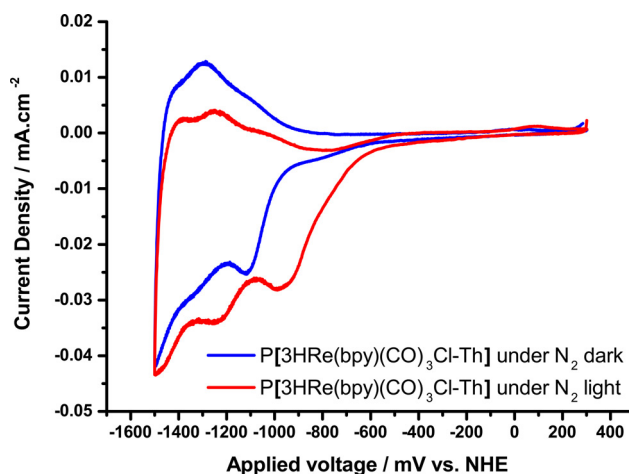


Figure 5. Cyclic voltammograms of $\text{P}[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ under dark and illumination in N_2 atmosphere.

related to bipyridine (around -900mV) and Re-centered electrochemical activity (around -1200mV) towards more positive values can be seen clearly in the cyclic voltammogram indicating the activity of the electrode under illumination.

For the characterization of $\text{P}[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ as a catalytic material for CO_2 reduction, both chambers were purged with CO_2 with the same flow rate and stirred vigorously at the same time for 45min. Figure 6 shows the electrochemical behavior of $\text{P}[3\text{HRe}(\text{bpy})(\text{CO})_3\text{Cl-Th}]$ under N_2 and under CO_2 respectively while the electrode in the cathode compartment was illuminated with a halogen lamp (Philips GU 5.3 50W, 12V 36D) with an IR glass filter in between. Intensity of the light in the vicinity of the cathode was measured using a calibrated Si cell and found as $60\text{mW}\cdot\text{cm}^{-2}$. Illumination is crucial since the backbone of the polymer consists of polythiophene which is known to be a p-type semiconductor.

The working principle of the polymeric catalyst is shown in Figure 7. When light is absorbed by the functionalized poly-

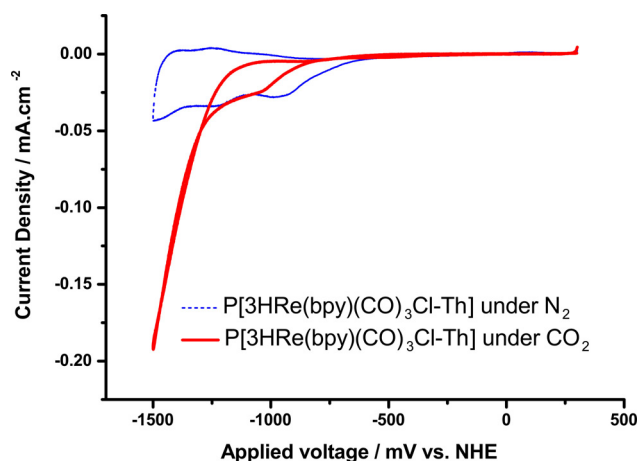


Figure 6. Electrochemical behaviour of P[3HRe(bpy)(CO)₃Cl-Th] in N₂ (blue dashed line) and CO₂ (red straight line) atmosphere under illumination.

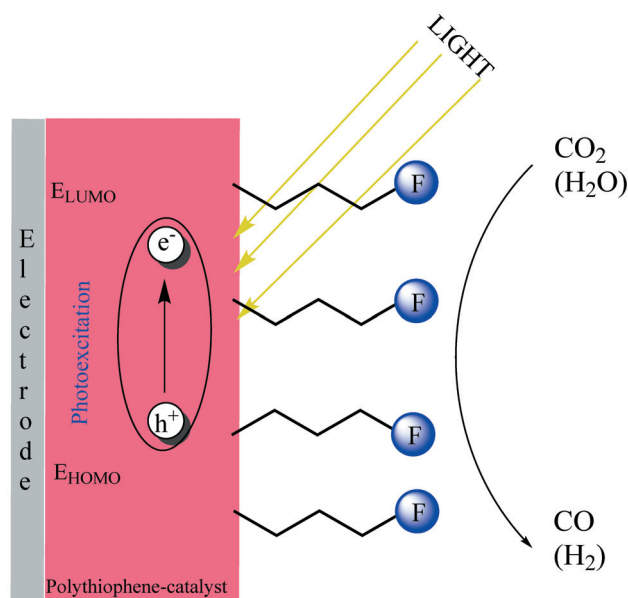


Figure 7. Working principle of the polymeric catalyst upon irradiation with light. H₂ can be observed as a product when the electrolyte medium is protic.

thiophene, an electron-hole pair, also called exciton, is generated. This exciton either recombines or in the ideal case travels to the electrode-electrolyte interface. If the driving force is strong enough, it dissociates, allowing the electron to be transferred to the catalyst that will facilitate CO₂ reduction. The remaining hole travels to the negatively biased electrode, where it will recombine with an electron to complete the circuit.

After the cyclic voltammety measurement, the H-Cell was purged with CO₂ again for an additional 15min with the same flow rate. A constant potential of -1500mV vs. NHE was applied for 3 hours both under illumination and dark separately. At the end of the electrolysis a sample of was taken from the headspace and injected to gas chromatography for the product

analysis. Since the electrolysis was carried out in an aprotic environment the expected product was CO^[8]. Repeated measurements under illumination yielded CO amounts ranging between 12-15 μ L (0.48-0.6 μ mol) while the amount of CO under dark conditions was < 1.5 μ L (0.06 μ mol). The highest Faradaic efficiency was found as 2.5% while the highest Turnover number (TON) was found as ~20. The low Faradaic efficiency and TON might be explained with the fact that only the species on the surface where electrode and electrolyte have an interface are active. With this in mind, the theoretical amount of active sites on the surface was calculated as 8.8×10^{-9} mol.cm⁻² [34,35]. These values are comparable with the literature values which examines the efficiency parameters in solution^[28]. Efficiency of such a system might be increased via the increase of above-mentioned interface and this can be realized through the polymerization of the film on a porous electrode like carbon felt. Using such a carbon electrode might also increase the efficiency due to a better energy level alignment. Pt has a work function of ~6.0eV^[36] whereas the polymer has a HOMO level (valence band) of 5.5 which is higher than that of Pt. This may lead to non-efficient hole transfer to the electrode which again might explain the lower efficiency. For the structural characterization of the product, another sample of 2mL was taken from the headspace and injected into a self-made transmission IR cell designed for gaseous substances^[12]. The structure of the product was confirmed as CO by the characteristic peak at 2143cm⁻¹ in all cases. At the end of 90min of electrolysis the color of the electrode started to turn to dark yellow and then brownish under dark conditions which might be an indication for decomposition since polymer backbone is not suitable for supporting electron transport.

Several studies from the Kubiak group showed, that water addition to the electrolyte system to have a mixture of MeCN/H₂O can increase the faradaic efficiency of the CO production.^[5,37] However, in our case the faradaic efficiency for CO production decreased severely upon addition of 5% of water (by volume) to the acetonitrile based electrolyte solution. We confirmed this by GC where we observe a decrease in the peak area of CO while we see another peak corresponding to H₂ is being evolved.

To prove the need of the combined work of polythiophene and catalyst material we performed the same experiment with an electrochemically grown thin film of P3HT. Controlled potential electrolyses were performed both under dark and under illumination. The headspace analysis with GC as well as IR measurement did not show any formation of expected products, CO being the major one. That concludes the necessary addition of the catalytic function to the backbone.

In the second pathway, following the work of Bocarsly on pyridinium catalyzed CO₂ reduction to methanol, our group published a paper describing a comparison between pyridine and pyridazine molecules^[20]. However, to the best of our knowledge no investigation has been done having the pyridine immobilized on a polythiophene electrode. The electrode having the structure of Pt/P[3HPyr-Th] was immersed in a solution of 0.5M KCl with Pt plate as a counter and Ag/AgCl (3M KCl) as the reference electrode. The pH of the solution was adjusted

with 1M H₂SO₄ solution to 5.2 prior to electrochemical experiments. No significant catalytic enhancement of the current was observed as in the case of P[3HRe(bpy)(CO)₃Cl-Th] which might be an indication for catalytic CO₂ reduction. Nevertheless we performed a controlled potential electrolysis keeping the potential constant at -550mV vs. Ag/AgCl. At the end of the electrolysis 1μL of solution was taken and measured in liquid injection gas chromatography which returned no detectable products.

Conclusions

We describe the synthesis and electrochemical characterization of two 3rd generation polymers and investigate their ability to reduce carbon dioxide to carbon monoxide. In the case of Rhenium bipyridine functionalized polythiophene we obtained a maximum Faradaic efficiency of 2.5% and TON of ~20. We show that the illumination of the electrode during the controlled potential electrolysis is a must in order to generate charge carriers facilitating photoelectrochemical reduction of CO₂. When 5% of water is added into MeCN to increase the Faradaic efficiency of the process, the reduction of protons to yield H₂ becomes more favourable and reduces the actual faradaic efficiency of CO production down to < 1%. Despite the fact that the observed faradaic efficiencies here are low, there is definitely room for improvement. The heterogeneous catalysis is heavily surface and diffusion limited, in general. Increasing the surface area of the electrode or using porous electrodes might be one way to go in order to increase the interaction of CO₂ with the catalyst. The 3rd generation conjugated polymers offer a neat way to alter the perspective of electrochemical/photoelectrochemical reduction of CO₂. Also the photophysical and photochemical electron transfer from the conjugated polymer backbone onto the catalyst group has to be optimized by engineering the HOMO-LUMO levels in the future.

Experimental Section

Experimental details considering the synthesis of monomers can be found in the supplementary information.

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Keywords: photoelectrochemistry · carbon dioxide reduction · Re complex · pyridinium · third generation polymers

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