Quinone-Pyrrole Dyad Based Polymers for Organic Batteries

From Design to Application

HAO HUANG
Organic electrode materials are finding increasing use in energy storage devices due to their attractive properties that allow building of flexible and low weight devices in an environmentally friendlier manner than traditional alternatives. Among these organic electrode materials, conducting redox polymers (CRPs), consisting of conducting polymer (CP) with covalently attached redox active pendant groups (PG), have attracted our interests. This is due to the advantageous synergy between CP and PG, e.g. electronic conductivity, high stability and large charge storage capacity. In this thesis polypyrrole has been selected as CP and quinones as PGs. A series of quinone-pyrrole dyad polymers has been synthesized with a variety of quinone substituents, demonstrating the adjustability of quinone formal potentials by choice of substituents. Importantly, in this series we show that the CP-PG redox match, i.e. that the formal potential of the PG is within the conducting region of the CP, is a requirement for fast charge transfer from the electrode to the PGs. Moreover, a series of quinone-pyrrole dyad polymers with various linkers was synthesized, showing that the choice of linker has a pronounced impact on the interactions between the PG and CP. In addition, the temperature dependence of conductance during doping of the polymers reveals the charge transport mechanism. To summarize, the adjustability of the quinone formal potential as well as the fast charge transport in the bulk material ensures the applicability of the CRPs as electrode materials in organic batteries.

Keywords: Organic battery, conducting polymer, quinone, polypyrrole, spectroelectrochemistry, conductance
To my parents
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


VI Huang, H.; Strømme, M.; Sjödin, M.; Gogoll, A., Potential Tuning in Quinone-pyrrole Dyad Based Conducting Redox Polymers. *Manuscript*.


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My contribution to the included papers

Paper I: I participated in the planning of the study, performed the monomer synthesis, was involved in writing the first draft of the manuscript and contributed to the continued writing process.

Paper II: I participated in the planning of the study, performed the monomer synthesis, was involved in writing the first draft of the manuscript and contributed to the continued writing process.

Paper III: I participated in the planning of the study, performed all the computations, synthesis and data analysis. I wrote the first draft of the manuscript and contributed to the continued writing process.

Paper IV: I participated in the planning of the study, performed the monomer synthesis, was involved in writing the first draft of the manuscript and contributed to the continued writing process.

Paper V: I participated in the planning of the study, performed all experimental work and data analysis. I wrote the first draft of the manuscript and contributed to the continued writing process.

Paper VI: I participated in the planning of the study, performed the all computations, experimental work and data analysis. I wrote the first draft of the manuscript and contributed to the continued writing process.

Paper VII: I participated in the planning of the study, performed the all the experimental work and data analysis. I wrote the first draft of the manuscript and contributed to the continued writing process.
Also published


XV Blom, M., **Huang, H.**, Gogoll, A. Photoswitchable peptidomimetics with a stiff-stilbene chromophore for inhibition of Mycobacterium tuberculosis RNR. *Manuscript.*
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<th>Description</th>
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<tbody>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflectance-flourier transform infrared</td>
</tr>
<tr>
<td>BQ</td>
<td>Benzoquinone</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CP</td>
<td>Conducting polymer</td>
</tr>
<tr>
<td>CRP</td>
<td>Conducting redox polymer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
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<tr>
<td>EDG</td>
<td>Electron donating group</td>
</tr>
<tr>
<td>EES</td>
<td>Electrical energy storage</td>
</tr>
<tr>
<td>EQCM</td>
<td>Electrochemical quartz crystal microbalance</td>
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<tr>
<td>ET</td>
<td>Electron transfer</td>
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<td>EWG</td>
<td>Electron withdrawing group</td>
</tr>
<tr>
<td>Fc</td>
<td>Ferrocene</td>
</tr>
<tr>
<td>GC</td>
<td>Glass carbon</td>
</tr>
<tr>
<td>HQ</td>
<td>Hydroquinone</td>
</tr>
<tr>
<td>IDA</td>
<td>Interdigitated array</td>
</tr>
<tr>
<td>IRAV</td>
<td>Infrared active vibration</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium-ion battery</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbital</td>
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<tr>
<td>PG</td>
<td>Pendant group</td>
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<tr>
<td>PAc</td>
<td>Polymethylene</td>
</tr>
<tr>
<td>PPy</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PS</td>
<td>Potential step</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>RM</td>
<td>Redox molecule</td>
</tr>
<tr>
<td>RP</td>
<td>Redox polymer</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SQ</td>
<td>Semiquinone</td>
</tr>
<tr>
<td>THP</td>
<td>Tetrahydropyranyl</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilyle</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
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### Important symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>SI unit</th>
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<tr>
<td>$A$</td>
<td>Area</td>
<td>$m^2$</td>
</tr>
<tr>
<td>$d$</td>
<td>Distance</td>
<td>$m$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
<td>$m^2/s$</td>
</tr>
<tr>
<td>$E$</td>
<td>Potential</td>
<td>$V$</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Standard potential</td>
<td>$V$</td>
</tr>
<tr>
<td>$E_0'$</td>
<td>Formal potential</td>
<td>$V$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap energy</td>
<td>$eV$</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>C/mol</td>
</tr>
<tr>
<td>$G$</td>
<td>Conductance</td>
<td>$S$</td>
</tr>
<tr>
<td>$i$</td>
<td>Current</td>
<td>$A$</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
<td>$eV/K$</td>
</tr>
<tr>
<td>$k^0$</td>
<td>Rate constant</td>
<td>$s^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>Number density of charge carriers</td>
<td>$m^{-3}$</td>
</tr>
<tr>
<td>$Q$</td>
<td>Charge</td>
<td>$C$</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
<td>$J/mol/K$</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Polymer resistance</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>$K$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>$s$</td>
</tr>
<tr>
<td>$v$</td>
<td>Scan rate</td>
<td>$V/s$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Conductivity</td>
<td>$S/m$</td>
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1. General introduction

Conducting polymers (CPs) are organic polymeric materials that have been widely used in many applications, such as electric energy storage,\(^1\),\(^2\) organic solar cells,\(^3\) organic light-emitting diodes,\(^4\) sensors,\(^5\) and transistors.\(^6\) Redox active molecules have also been suggested as active battery materials because of their high specific energy.\(^7\) However, dissolution of small molecules in the electrolyte leads to self-discharge as well as poor cycling performance,\(^8\) which limits the usage of redox molecules as electrode materials in battery applications. To solve this problem, we have proposed conducting redox polymers (CRPs), in which redox active moieties are employed as pendant groups (PGs), covalently grafted onto the CP. The use of CP as polymeric matrix to a large extent decreases the solubility of the material and at the same time improves its conductivity, with better performance as the expected result.

To explore the compatibility of CPs and PGs in the composition of CRPs, a series of CRPs has been synthesized, using quinones as PGs and polypyrrole (PPy) as backbone. The redox activities as well as the charge transfer process in these materials are our main interest. Furthermore, elucidation of the interactions between the CP and PG units during electrochemical processes is of importance for improvement of CRP designs. Finally, the construction of fully organic material based batteries using CRPs as electrode materials is the ultimate goal of this work.

The particular objectives of the work presented in this thesis are summarized in the next chapter, followed by an overview of the major techniques involved. Background knowledge about energy storage materials is given in chapter IV. In chapters V and VI, a more specific description of the work covered in this thesis is provided, including results and discussion. Conclusions and perspectives of this work are summed-up in the final chapter.
2. Aim of the thesis

The work presented in this thesis has the aim to investigate the electrochemical properties of quinone-pyrrole dyad based polymers and how these can be modulated by the chemical architecture. Thus, the redox activity of the quinone pendant group, the interaction between the pendant quinone and the PPy backbone as well as the mechanism of charge transport in the material has been studied. Providing guidelines for modulating the properties of quinone based CRPs is the essence of this work, facilitating the possibility of using this material as electrodes in fully organic matter based batteries.

The specific objectives of this work, described in the included papers, are listed as follows:

- To provide synthetic protocols for access to quinone-pyrrole dyads with various linkers as well as various quinone substituents (papers I, III and VI).

- To investigate the interaction between CP and PG in CRPs upon oxidation of the PGs (papers II, IV and V) and the influence of the choice of linkers (papers III and IV).

- To explore the redox activity of quinones as PG in CRPs and the compatibility between CP and PG (paper VI).

- To study the mechanism of charge transport in CRPs during the doping process of the CP (paper VII).
3. Overview of employed methods

3.1 Electrochemical methods

Electrochemistry is used for characterizing electronic materials since it reveals the chemical reactions resulting from applying voltage or current. An electrochemical measurement is typically conducted in an electrochemical cell where electric current - potential relationships for redox reactions are recorded.

3.1.1 Three electrode set-up

An electrochemical experiment often involves a three electrode set-up in the presence of an electrolyte. A controlled potential is applied to the working electrode (WE) to electrify the analyte. The analyte may be molecules dissolved in the electrolyte, or electroactive materials coating the surface of the WE. A counter electrode (CE) is used to form the other half of the electrochemical cell, balancing the charge added to or removed from the WE. Occasionally a separate compartment for the CE is required to prevent electrochemical reactions occurring at the CE from causing changes in the electrolyte. A reference electrode (RE) consisting of a redox couple with a known and well defined redox potential is the third electrode in this set-up. It acts as a reference for controlling and measuring the potential of the WE, and no current should pass through the RE at any time. The recorded potential for the investigated electrochemical reaction is referred to this RE and it may be converted to other reference systems. For better comparison with other studies potentials in this thesis are referenced to the standard hydrogen electrode (SHE) and to the ferrocene redox couple (Fc\(^{0+/+}\)) in aqueous electrolyte and in organic electrolyte respectively.

3.1.2 Cyclic voltammetry

As one of the most important technique in electrochemistry, cyclic voltammetry provides electrochemical properties of analyte in solution. In a cyclic voltammetry experiment the WE potential is ramped linearly versus time (Figure 1a) to the set potential, followed by ramping it reversely back to the initial potential. During this process, the current response is recorded. This potential sweep may be repeated several times. When the analytes start to
react the measured current will change accordingly, which can be seen in the cyclic voltammogram (CV). During potential sweep towards higher potentials electrons are withdrawn from the analyte to the WE, corresponding to oxidation. On the reverse scan, the WE potential is lowered and the current response is associated with reduction of analyte. Figure 1b shows a CV of ferrocene dissolved in MeCN. Taking the forward scan as an example, at low potentials there are no changes of current. When the potential reaches 0 V vs Ag/Ag⁺, the current starts to increase, reaches the peak current and then decreases. The tailing of CV curve after the peak current is because the analyte is gradually consumed around the WE and it takes some time for more analyte to be transported to the WE. It is common practice to report the mean value of the forward and backward peak potentials as the formal potential of the redox reaction.

In a reversible reaction where the reaction is fast enough to maintain the concentration of reduced and oxidized species at the electrode in equilibrium state, and the equilibrium ratio is given by the Nernst Equation:

\[
E = E^0 - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right)_{x=0}
\]

where \(E\) is the potential, \(E^0\) is the formal potential, \(R\) is the gas constant, \(T\) is the temperature, \(F\) is the faraday constant, \([R]\) is the concentration of reduced species and \([O]\) is the concentration of oxidized species.

In an alternative set-up, the species under investigation may be attached to the WE surface and thus exhibiting a different CV. If the layer of the species of interest is sufficiently thin, making the redox process non-diffusion limited, the observed voltammogram is symmetrical with peaks of Gaussian peak shape and peak separation between the oxidation and reduction peaks is negligible (Figure 1c).

From a CV with the charges \((Q)\) passing through the electrodes can be obtained by integrating current over time \((Q=\int i \, dt)\). With a constant scan rate \((v=\frac{dE}{dt})\), the charge can be calculated by transforming the formula as shown below:
\[ Q = \int i \, dt = \int i \, \frac{dt}{dE} \, dE = \int \frac{i}{v} \, dE = \frac{1}{v} \int i \, dE \quad (2) \]

Therefore, the charge is obtained as the integral of the CV peak divided by the scan rate.

By adjusting parameters such as scan rate and pH of the electrolyte, a CV measurement can reveal information about the reaction kinetics. This will be discussed in more detail later.

### 3.1.3 Chronoamperometric method

In contrast to a CV measurement where the potential of the WE is increased linearly to certain predetermined value, the chronoamperometric method involves stepwise potential change to selected values, and the current passing through the electrode is recorded as a function of time. This so called potential step (PS) voltammetry is also a useful technique in electrochemistry to determine reaction kinetics. In this thesis it was mainly used as an alternative method of polymerization.

### 3.1.4 Two-electrode measurements

Sometimes a two electrode set-up instead of a three electrode set-up is used in electrochemical experiments. In two electrode measurements, there are only a WE and a CE. The potential between these two electrodes is monitored and thus the device can be cycled in a controlled cell potential region. It is widely used for the measurements in devices where whole cell is measured, for example, batteries, fuel cells and supercapacitors. Unlike to a three electrode measurement in which the WE potential is checked against the RE and the potential between WE and CE is unknown, two electrode experiments measure the potential difference between the two WEs. As the redox chemistry of both WEs might influence each other during the measurement, two-electrode measurements might not reflect the sum of individual performance of the two WEs in a three-electrode measurement respectively. Moreover, an external RE would also be connected to one or both of the electrodes via a voltmeter to monitor the potential change of the WEs against a known reference.

### 3.2 In situ techniques

In situ is Latin for “on site”. When applied to techniques used in electrochemistry it refers to measurements at the very place where the investigated phenomenon is occurring. In other words after an induced change in the analyte the response is recorded at the same location at which the change has
been triggered. In this way there is no need to isolate the object of interest from the system prior to measurement, thus avoiding the risk of further changes on its way to the location of measurement. For in situ techniques in characterization of polymeric materials electrochemical experiments may be combined with spectroscopic measurements, such as Fourier transform infrared spectroscopy (FTIR) and ultraviolet-visible (UV-vis) spectroscopy to study optical properties of the material, as well as with other measurements, such as electrochemical quartz crystal microbalance (EQCM) experiments and conductance measurement.

3.2.1 In situ ATR-FTIR

Attenuated total reflection FTIR (ATR-FTIR) spectroscopy has been extensively used for in situ studies of liquid or solid samples. ATR-FTIR is a sampling technique that allows the non-invasive measurement of intensity changes of IR light interacting with a material. In this set-up, IR light when reflected inside of a crystal at its surface produces an evanescent wave that protrudes a small distance beyond this surface, thus penetrating any material in close contact with the surface. The remaining light is collected by a detector when it exits the crystal.\(^{[10]}\)

In this work, ATR-FTIR combined with electrochemical measurements was employed to monitor the spectroscopic response from a polymer during the electrochemical process. Details of the cell set-up are shown in Figure 2.

![Figure 2. Schematic diagram of in situ ATR-FTIR set-up for spectrochemical measurements. The polymer was polymerized in the same cell and then measured on. A Pt foil conjunct to the surface of WE was used as an extension of WE to provide a connection between the WE and the working station.](image)

3.2.2 In situ UV-vis spectroscopy

UV-vis spectroscopy has been an essential tool in characterizing organic compounds as it may reveal structural or electronic changes of molecules if these alter the energy levels involved in electronic excitation. When it comes to combination with electrochemistry techniques such as CV or PS, in situ
UV-vis spectroscopy provides information on changes of analyte chromophores resulting from redox reactions or degradation reactions during electrochemical processes.

In our studies, polymers were polymerized electrochemically onto a WE consisting of an indium tin oxide coated quartz slide. The slide was placed in a quartz cuvette where the CE and RE are also located (Figure 3).

![Figure 3. Schematic illustration of set-up of in situ UV-vis spectroelectrochemical measurement.](image)

### 3.2.3 In situ EQCM

The EQCM measurement provides a technology widely applied to processes involving structural and/or compositional changes at the interfaces in electrochemistry.[11] It employs the piezoelectric effect, i.e. a mechanical stress applied to a crystal surface generates an electrochemical potential response across the entire crystal, with the magnitude of the potential response being proportional to the applied stress.[11] Conversely, the application of a potential across the crystal generates a corresponding mechanical stress, which induces oscillations. As mass deposits on the surface of the quartz crystal the induced oscillation changes and the change in oscillation frequency \( \Delta f \) that results from a mass deposited onto the crystal is given by

\[
\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\mu_q\rho_q}}
\]

which is the Sauerbrey equation,[11] where \( \Delta f \) is the measured frequency shift, \( f_0 \) is the oscillation frequency of the crystal, \( \Delta m \) is the mass change, \( A \) is the piezoelectrically active area, \( \rho_q \) is the density and \( \mu_q \) is the shear modulus of quartz.

In EQCM the thin quartz crystal is placed between two electrodes that provide an alternating electric field across the crystal, initiating the oscilla-
tion of the crystal at its resonant frequency. One of these electrodes is employed as the WE in an electrochemical cell. This allows to measure mass changes of the electrode-quartz crystal-WE wafer via the change of oscillation frequency. In order to apply the Sauerbrey equation when interpreting the frequency change some assumptions had to be made. For example the polymer deposited on the crystal must be being uniformly distributed on the active area and the density of the polymer must be homogenous across the entire film. Moreover, the film is assumed to be rigid during redox cycling, ignoring the changes in morphology and swelling of the polymer during the ingression and egression of counter ions and solvents.\[^{[11]}\]

3.2.4 In situ conductance

Conductivity is an essential feature of CPs, allowing the materials to be applied in many areas. A closer investigation of the CP conductivity should provide further understanding of the charge transfer from a mechanistic perspective, allowing improved design and construction of CPs. Also, it might broaden the application of such materials if characteristic responses in terms of varied conductivity under certain physical stimulations, e.g. temperature changes or irradiation can be realized. In situ conductance measurements can provide information on such conductivity variations, which is difficult to achieve by ex situ measurements.

A set-up of two WEs was used in the measurement of in situ conductance for the synthesized polymers.\[^{[12]}\] After electrochemical polymerization from a monomer solution, the polymer was coated onto the electrode surfaces, thus covering the gap between two WEs (Figure 4a). A potential bias (\(E_{\text{bias}}\)) was applied over these two WEs and the current passing through each WE was monitored. The current passing through the two WEs is denoted as \(i_1\) and \(i_2\) respectively, and the current passing through the polymer is denoted as \(i_p\). The faradaic current flows through each WE is denoted \(i_{F1}\) and \(i_{F2}\). Thus the current passing through the polymer (\(i_p\)) can be obtained from the bias potential (\(E_{\text{bias}}\)) and the resistance of the polymer coated WE (\(R_p\)) by applying Ohm’s law as:\[^{[13]}\]

\[
i_p = \frac{E_{\text{bias}}}{R_p} \tag{4}\]

According to the Kirchhoff’s circuit law,\[^{[13]}\] i.e. the sum of currents flowing into the node is equal or equivalent to the sum of the current flowing out of that node. Taking node A and B in Figure 4, we obtain

\[
i_1 + i_p = i_{F1} \tag{5}\]
\[
i_2 = i_p + i_{F2} \tag{6}\]

Eq.[6] – Eq.[5],

\[
i_2 - (i_1 + i_p) = i_p + i_{F2} - i_{F1} \tag{7}\]
then
\[ i_2 - i_1 = 2i_F - 2i_{F_1} \]  
\[ (8) \]
Letting \( \Delta i = i_2 - i_1 \) and \( \Delta i_F = i_{F_2} - i_{F_1} \), thus we get
\[ \Delta i = 2i_P + \Delta i_F \]  
\[ (9) \]
to keep the scan rate slow enough in order to minimize the \( \Delta i_F \), therefore we have \( \Delta i_F << i_P \), allowing \( \Delta i_F \) to be negligible, then
\[ i_P = \frac{\Delta i}{2} \]  
\[ (10) \]
Thus the conductance \( (G, \text{the inverse of resistance}) \) can be calculated by
\[ G = \frac{1}{R_p} = \frac{i_P}{E_{bias}} = \frac{\Delta i}{2E_{bias}} \]  
\[ (11) \]
The set-up of two WEs is realized by using interdigitated array (IDA) electrodes in which each WE consists of 90 gold strips as shown in Figure 4b. The dimensions of the electrodes are known, it is, however, difficult to measure the accurate geometry of the coated polymer and thus the calculation of absolute conductivity of the polymer from conductance is not trivial. Nevertheless, by assuming that the polymer was covering the entire active area, the conductivity \( (\sigma) \) can be estimated by knowing the distance between the two WEs \( (d) \) and assuming the electrode side surface area \( (A) \) as the cross section area through the direction of current flow:
\[ \sigma = G \frac{d}{A} \]  
\[ (12) \]
Figure 4. a) Circuit diagram of a two WEs set-up for in situ conductance measurement, together with a RE and a CE extensionally to construct a four electrodes cell. A bias potential was applied over the two WEs, and the polymer coated onto the gaps between the WEs, giving the resistance \( R_p \); b) Illustration for an IDA electrode with showing the electrochemically active area only.
4. Energy Storage Material

Climate changes and dwindling energy resources have become major driving force for achieving a sustainable development of society.[14] Fossil fuels, which have a large negative impact on climate changes and pollution, supplied approximately 68% of the electrical energy worldwide in year 2008.[15] Because of the decreasing availability of petroleum and the environmental concerns of fossil fuels, finding sustainable alternative energy resources has become an increasing concern. Solar and wind power are the most pronounced renewable energies because of their great abundance and readily accessibility.[15] However, they are subject to pronounced temporal fluctuation in availability. Therefore, these energy sources cannot guarantee a continuous supply which makes supplementary solutions necessary. Electrical energy storage (EES), i.e. conversion into and storage of energy in chemical form, followed by release of energy in electrical form may provide a buffering period between energy generation and energy consumption thus promoting a more efficient way of utilizing electricity generated from intermittent sources.

The use of batteries is essentially connected to our daily lives and industrial production.[16] Amongst batteries, rechargeable lithium ion batteries (LiBs) have been extensively studied and developed to have the highest market shares in portable batteries, owing to their high energy density resulting from high specific capacity and high voltage.[17] Considering the limited availability of metals in nature, and also the huge amount of energy required for exploitation as well as recycling of metals, a high carbon footprint is associated with LiBs. Organic material based electrodes, on the other hand, obtainable from abundant raw materials from nature, and not involving harmful or toxic metals should provide an alternative to currently dominating inorganic electrode materials.

Figure 5 illustrates the concept of adapting organic material based battery devices as integral parts of the energy infrastructure. By selecting abundant materials from renewable natural sources, followed by chemical modifications by organic synthesis, suitable organic materials for energy storage might be accessible. Such materials are expected to have low carbon emission, lower toxicity as well as structural flexibility. When an organic matter based device meets its due time, recycling could be readily achieved by combustion.
4.1 Characteristics of batteries

A battery is a device consisting of one or several electrochemical cells with contacts or terminals to provide electrical energy. In a battery, the energy is stored in chemical form that can be converted into electrical energy via redox reactions. Depending on the restorability of the electrochemical cell, batteries can be divided into two classes: primary batteries in which discharge is the primary process during operation, and secondary batteries where the cell after discharging can be restored to its original status by reversing the current flow through the cell.

There are three principle components in a battery: the electrodes (anode and cathode) and the electrolyte. In a primary battery where only discharging occurs, the anode is the negative electrode that is oxidized and releases electrons into the external circuit, whereas the cathode (the positive electrode of an electrochemical cell) is reduced and obtain electrons from the external circuit during discharge. In a secondary battery, the direction of current flow reverses between the charging and discharging process. For clarity, throughout this thesis the anode is defined according to discharging process. Concerning the electrolyte, it is the material that provides the ionic conductivity between the anode and cathode in a cell (Figure 6).
The voltage ($V$) of the cell is determined by the potential difference between the two electrodes, namely cathode and anode.

$$\text{Cell voltage (V) = Cathode potential – Anode potential} \quad (13)$$

The theoretical capacity ($C_{\text{theo}}$ [Ah]) is the maximal electrical charge that can be stored in the cell with full utilization of the active material in the limiting electrode. The unit for capacity is coulomb (1 C = 1 As) or Ah (1 Ah = 3600 As). In order to compare different electrodes, a theoretical specific capacity is used ($C_s [m \text{Ah}^{-1}]$ ) which gives the theoretical capacity of the electrode per mass of active material and can be calculated according to

$$C_s = \frac{n \times F}{M_w} = \frac{n \times 96485 [\text{As} \text{mol}^{-1}]}{M_w [g \text{mol}^{-1}]} = \frac{n \times 26801}{M_w} [m \text{Ah}^{-1}] \quad (14)$$

where $n$ is the number of electrons transferred during the redox reaction, $F$ is the Faraday constant, and $M_w$ is the molar mass of the redox active material. Redox active materials with low molecular weight are thus essential for obtaining high capacity in batteries.

Combining the theoretical capacity ($C_{\text{theo}}$) and the voltage ($V$) gives the theoretical energy ($E_{\text{theo}}$ [Wh]) which defines the maximum energy that can be delivered by a cell (Eq.[15]). As for the specific capacity, for comparing different cells, a specific energy ($E_{\text{spec}}$ [Wh g$^{-1}$]) is usually given by dividing the maximum energy that a cell can deliver by the mass of the capacity limiting active material.$^2$

$$E_{\text{theo}} = C_{\text{theo}} \times V \quad (15)$$

4.2 Small organic redox molecules

Organic redox molecules (RMs) that undergo reversible electrochemical redox reactions can potentially be used as active electrode materials in a battery, offering alternatives to inorganic electrode materials. Commonly
used organic redox molecules usually have low molecular weight and thus a high capacity is expected.

There are several types of small organic molecules that have been studied as possible EES materials and their properties are presented in Figure 7. For instance, organosulfur compounds\textsuperscript{[20],[21]} such as disulfides exhibit interesting redox properties by breaking and reforming the disulfide bonds. Generally high theoretical capacities have been obtained from these materials since disulfide bond allow for a two electron redox reaction.\textsuperscript{[22],[23]} However, sluggish kinetics for the S-S bond breaking and reformation are often found in this type of EES materials. Besides such disulfides, radicals and carbonyl compounds have also shown great potentiality for application as cathode materials in EES. The well-studied radical compounds for this purpose are based on nitroxides. Among these, 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) is certainly the most reported nitroxide for EES.\textsuperscript{[24],[25]} Fast kinetics and stable cyclability were found for electrode cells based on this material. However, the charge capacity of such radical cells is limited by the number of electrons that can be stored per monomer unit as well as the high molar mass of these molecules.\textsuperscript{[26]} Conjugated carbonyl compounds are among the earliest organic candidates for electrode materials in LiBs. High capacities may be achieved by a proper molecular design, rendering carbonyl compounds one of the most promising organic electrode materials yet. Quinones have been suggested as cathode materials for their reversible redox chemistry and relatively high redox potential.\textsuperscript{[27],[28]} Furthermore, conjugated dicarboxylates, another type of carbonyl compounds, have been used as anode material for LiBs,\textsuperscript{[29],[30]} as they have low redox potentials.

One major problem with small organic molecules as electrode materials is the dissolution of active material into the electrolyte, resulting in self-discharging as well as poor cycling performance.\textsuperscript{[8],[31],[32]} By contrast, constructing a polymer incorporating these active moieties that is insoluble in the electrolyte is likely to solve these problems.
4.3 Conducting Polymers

Polymers are macromolecules that consist of repeating structural subunits. Conducting polymers (CPs) are a subset of organic polymers that exhibit intrinsic electrical conductivity. Since the first discovery of conductive polyacetylene (PAC) films in the late 1970s\textsuperscript{[33]} by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, awarded the Noble Prize in chemistry in 2000, CPs have received great attention in research as well as in industrial applications. In the past 30 years, as a result of their outstanding electrical and optical properties, CPs have been used in a number of applications including energy storage,\textsuperscript{[1],[2],[34],[35]} biosensors,\textsuperscript{[36]} photovoltaics,\textsuperscript{[37]} actuators\textsuperscript{[38]} as well as polymer light emitting diodes (LEDs).\textsuperscript{[39],[40]}

4.3.1 Doping induced conductivity

Organic polymers, generally known as plastics, are typically electronic insulators which have been used as insulating layers covering conductive metals to prevent shortcuts. However, upon ‘doping’ the electronic properties of the CPs are converted to become conductive. “Doping” is a term borrowed from the semiconductor field, describing a process of introducing electron-deficiency to the valence band (VB) or electron-excess to the conduction band (CB) in order to modulate the electrical properties of a material. When applied to CPs it usually refers to the oxidation or reduction of CPs. With oxidation (referred to as p-doping) or reduction (referred to as n-doping) of CPs, electrons are removed from the top of the VB or added to the bottom of the CB, respectively. Radical cations or radical anions, so called polaron, are therefore generated.\textsuperscript{[41]} In order to uncover the reason why CPs, in con-
trast to conductors, require doping, it is important to understand the electronic structure of CPs and also the structural changes during the redox conversion.

Conducting polymers are generally composed of conjugated bonds with alternating single and double bonds along their backbones. When two atoms combine to form a molecule, their atomic orbitals overlap and generate molecular orbitals (MOs) including bonding orbitals and anti-bonding orbitals. With more atoms involved in the bond formation, more MOs are generated and the energy gap between the bonding and antibonding MOs becomes smaller. Then reaching a certain extent, the combined MOs can be regarded as a band. The bonding orbitals constitute the valence band (VB), and the collection of antibonding orbitals gives the conduction band (CB). The energy gap \( E_g \) between the VB and the CB defines the electronic properties of the formed (macro)molecule. Following the Boltzmann distribution, the fraction of electrons in the CB is given by \( e^{-\frac{E_g}{kT}} \), if \( E_g \) is large it is unlikely to excite electron transitions from the VB to the CB thermally. Therefore the material is considered an insulator. If \( E_g \) is relatively small, we could have a semiconductor. For an intrinsic semiconductor, \( E_g \) cannot be much larger than \( kT \) (\( k \) is the Boltzmann constant, \( T \) is the temperature), e.g. at room temperature, \( kT = 26 \text{ meV} \).[42] If the \( E_g \) is zero, then we have a conductor. Metals with unfilled electronic valence shells are typical conductors because the electrons may move into unoccupied orbitals without requiring an increase in energy.

The simplest chemical structure of a CP, PAc with the chemical formula \((-\text{CH}=\text{CH}-)_n\), is a good example to demonstrate the conduction mechanism.[42] By assuming there is a linear \( \pi \) system along the whole PAc backbone with every C-C bond equivalent, the formed VB and CB get closer and closer as the size of the system increases. If the system is big enough, the band gap eventually disappears which could yield a metal conductor (Figure 8a). Since neutral PAc is not a conductor at room temperature, there must be a band gap between VB and CB and hence the assumption is not entirely true. In fact, PAc undergoes a geometrical distortion from a structure with equal bond length to a structure with alternating long and short bonds. This geometrical distortion is called Peierls distortion, and it also is identified as Jahn-Teller distortion as observed in cyclobutadiene. This geometrical distortion results in a band gap in PAc (Figure 8b). After being oxidized by removing one electron, the polymer undergoes ‘doping’ where a radical cation is generated(Figure 8c).[41] It is energetically favorable to localize the charges along the polymer chain resulting in localized electronic states formed in the band gap (Figure 8d). Further oxidation leads to the formation of more polarons or in the generation of dication species by the removal of unpaired electrons from the polaron state (bipolarons, Figure 8e). A polaron possesses a spin of \( \frac{1}{2} \) and thus it is detectable by EPR, whereas a bipolaron is spinless.[41] The evolution of these two species in CPs has been monitored
by various spectroelectrochemical methods,\cite{43,44,45} and it has been concluded that either of these two species could be the charge carriers giving rise to the conductivity of CPs.\cite{45,46} The doping induced conductivity is well demonstrated by an \textit{in situ} conductance measurement of polythiophene where the conductance of polythiophene increases upon the doping of polymer by either oxidation (p-doping) or reduction (n-doping).

Figure 8. The evolution of the chemical structure and band structure of PAc at different doping states. a) PAc with equal bond length and delocalized electrons in the conjugated $\pi$ system. b) Peierls distortion results in alternating long and short bonds along the backbone as well as a band gap. c) A hole in VB is generated upon oxidation. d) Relaxation of charges along the chain leads to the formation of a polaron. e) Further doping/oxidation results in that bipolarons are formed.
4.3.2 Charge transport

The mobility of the polaron or bipolaron along the chain gives rise to the conductivity. As expressed in eq.[16][47] the conductivity is related to the number density of charge carriers \(n\), the electron mobility \(\mu\) and the charge of the charge carrier \(q\). To increase the conductivity, one needs to increase the number of charge carriers and the mobility of the charge carriers.

\[
\sigma = n\mu q
\]  

(16)

The macroscopic conductivity depends on many parameters, e.g. the doping level, conjugation length, inter-chain interaction, degree of disorder etc. Most of these factors are subject to the morphology of the polymer and therefore the morphology of the formed polymer is the key term accounting for the degree of conductivity.[48] With variations of preparation methods as well as doping methods[49] the formed polymer in its solid state may either arrange in a disordered manner or self-assemble into crystalline segments over the whole material.[50] The degree of disorder in CPs results in different pathways for the polarons or bipolarons to migrate in terms of inter- or intra-chain transfer. At a certain doping level in a disordered bulk CP the inter-chain electronic coupling is weak and thus the polarons or bipolarons are localized on one chain, resulting in low conductivity. On the other hand, in crystalline domains of polymers, further electronic coupling is feasible among different chains due to extended orbital overlapping, which allows the polaron or bipolaron to delocalize through neighboring chains. It was
found that with increasing crystallinity in a bulk polymer, the coupling among inter-chains becomes stronger, thus the inter-chain electron transfer is so sufficient that the intramolecular electron transfer becomes rate limiting.\[51\] By tuning the degree of disorder in the polymer the material can undergo a transition from fermi-glass to metallic in terms of conductivity.\[52\]

4.4 Redox polymers

Redox polymers (RPs) is a group of polymers with non-conjugated backbone and with redox centers, i.e. RMs, localized in pendant groups covalently attached to the backbone.\[53\],[54],[55]\ In some cases, the redox center may also be part of the backbone.\[56\],[57]\ In RPs, the potential of the material is determined by the redox active groups, giving a distinct redox potential by assuming there are no interactions among the redox centers. Unlike CPs in which the doping induced conductivity facilitates the electron transfer, RPs have to rely on the electron hoping between the redox sites. The charge propagation via electron hopping is attributed to the concentration difference of the oxidized and reduced species.\[58\] Around the formal potential of RP the concentration of the oxidized and reduced species show the strongest dependency of potential and the conductivity will be at a maximum.\[59\] Since there is only a limited potential region where the concentration of the oxidized and reduced species is sufficiently affected by potential to promote conductivity, the operating potential window of RPs is limited.\[60\] As RPs allow access to a variety of polymers that cover a large range of potentials, they show great potential to be active materials in EES.\[61\],[26]\ Nevertheless, due to low conductivity in such materials excessive amounts of conductive additives have to be added to a device to achieve sufficient conductivity which lowers the volumetric as well as specific energy density.

4.5 Conducting redox polymer

A polymer that consists of CP as backbone and RMs covalently attached to the CP as pendant groups (PGs) constitutes a so-call conducting redox polymer (CRP). In a CRP, the conducting polymer backbone provides the conductivity upon doping. The redox molecules, attached to the polymer backbone as pendant groups, afford the redox activity offering charge capacity at fixed formal potentials. Being polymeric CRPs, in principle, do not easily dissolve in the electrolyte and thus better cycling stability as compared to small RMs is to be expected. This type of materials has been investigated in several potential applications, including EES,\[62\],[63]\ transistors,\[64]\ and sensors.\[65],[66]\ Various functional groups have been incorporated into CPs, e.g. porphyrin,\[67],[68]\ ferrocene,\[60],[69]\ quinones,\[70],[71],[72]\ other carbonyl compounds,\[73],[74]\
viologens$^{[75]}$ and nitroxide radicals$^{[66],[76]}$ demonstrating the applicability of this concept. However, the properties of these polymers, in general, have not been studied systematically, especially regarding the correlation between structure and properties as well as the compatibility between the PG and the CP. Therefore, the design principles of this type of polymer for application in energy storage still remain to be investigated and elaborated.
5. Quinone-pyrrole Conducting Redox Polymers

In CRPs it is often desirable to preserve the individual contributions of the CP and the PG to the operation of the CRP to attain advantageous synergic effects of these two units. There are three principal components in CRPs: the CP backbone, the PG and the linker between CP and PG. The combination of CP and PG should follow the redox matching principle, i.e. the PG redox reaction must occur within the conducting potential region of CP. For a p-doped CP the formal potential of PG should be above the doping on-set potential of the CP whereas for an n-doped CP, the formal potential of the PG should be below the doping on-set potential of the CP. The linker not only provides the attachment of the PG to the CP, but it also governs the interactions between the CP and the PG. A short linker, for instance, increases the steric hindrance between PGs which, as will be described in 5.4, leads to the twisting of the CP backbone, causing poor conductivity. In addition, in designing CRPs for application in energy storage, it must be considered that their specific capacity is related to the molecular mass, e.g. heavy substituents on the PG and long linkers should be avoided.

In this project, polypyrrole (PPy) is chosen as the CP backbone and quinone moieties serve as PGs in the CRPs investigated. The properties of CRPs with quinone moieties with various potentials, as accomplished by substitution on the quinone ring, as well as the interaction between the PG and CP upon varying the linker are investigated.

5.1 Polypyrrole

The first study of PPy was reported by Weiss at al. in 1963, in which the chemical structure and the electrochemical as well as the electronic properties were investigated. Since the discovery of high conductivities of doped PAc in 1977, research on conjugated polymers have attracted significant attention. Amongst these, owing to its easily synthetic availability, high conductivity and stability in its oxidized state, PPy has been extensively studied. PPy consists of repeating units of pyrrole in which the α-carbons are connected, forming a poly-conjugated π-system. The extended π-system gives rise to the optical properties of this type of material, which makes it
particularly interesting. Conjugation relies on the overlap of the \( \pi \)-orbitals of the heteroaromatic pyrrole rings which requires co-planarity between the connected pyrrole units. Twisting between the pyrrole units over the bond connecting them would break the co-planarity and thus reduce the conjugation length, causing low conductivity.\[^{[83]}\]

5.1.1 Polymerization of pyrrole

Polymerization of pyrrole is usually achieved by addition of an oxidizing reagent or by electrochemical oxidation. For example, chemical oxidation is achieved using reagents such as FeCl\(_3\) or Fe(ClO\(_4\))\(_3\). Upon oxidation the pyrrole monomer loses one electron and forms a cation radical (Figure 10). This radical cation has significant spin density at the \( \alpha \)-carbon\[^{[84]}\]. Two radical cations may react, forming a bond between their respective \( \alpha \)-carbon, giving a di-cationic dimer. Deprotonation restores the aromaticity and results in the formation of a neutral dimer (Figure 10). Further polymerization proceeds via consecutive dimerization of the dimers followed by dimerization of tetramers, etc. As the polymer chain grows the reactivity of the generated oligomers decreases. Therefore, polymerization becomes progressively more difficult and eventually chain propagation ceases. In addition, as the polymer chain gets longer, the solubility decreases, resulting eventually in precipitation from the solution, thus preventing further reaction. In electrochemical polymerization the polymer may precipitate onto the WE surface, forming a polymer layer on the WE.

![Figure 10. Scheme of the proposed mechanism of pyrrole polymerization with sequential steps i) oxidation ii) dimerization of radical cations and iii) deprotonation.](image)

5.1.2 Electrochemistry of Polypyrrole

The intrinsic redox reaction in PPy is associated with the doping and dedoping of the polymer. Upon oxidation, one electron is removed from the polymer and a radical cation is formed which is counterbalanced by accessible anions from the electrolyte. This process is referred to as polymer doping. In the reverse process called dedoping, the anions leave the polymer matrix when the polymer is reduced back to neutral state (Figure 11). The doping level denotes the number of charges generated per monomer unit and it increases with applied potential. The maximum doping level of PPy in aqueous electrolyte is found to be 0.25 -0.33, i.e. one charge per 3 to 4 pyrrole units, and is limited by over-oxidation of PPy at higher potential.\[^{[85]}\]
Figure 11. Doping process of PPy showing the oxidation by removal of electron from polymer backbone resulting in a radical cation polymer, corresponding to the polaron state of PPy. Further oxidation will lead to the formation of bipolarons. After reduction of a doped PPy, the polymer returns to the neutral state. This process is referred as dedoping.

A CV together with the *in situ* conductance of PPy is shown in Figure 12. The CV response is typical for all CPs; at a certain potential the polymer starts to dope and the current increases rapidly. Following the rapid current increase a current plateau is reached where a steady current with increasing potential is observed, resembling a capacitive response. The steady current implies that there is certain communication among the redox sites along the polymer. A higher potential is needed to further oxidize the segments of already oxidized polymers because of the increased coulombic interaction between the charged segments. In addition, different segments of the polymer might have different oxidation potential due to the different local environment. The *in situ* conductance measurement shows that before doping of PPy the conductance is nearly zero, which coincides well with the neutral state of PPy at this potential. As the potential reaches the on-set of PPy doping the conductance starts to increase and then reaches a steady state similar to the current in the CV. The steady conductance shows that it is independent of doping level at these potentials, suggesting that the number of charge carriers, and their mobility, is independent of doping level.[86]
5.2 Quinones

Quinones are, according to IUPAC, a series of compounds that have a fully conjugated cyclic dione structure which are derived from aromatic compounds by altering an even number of −CH= groups into −C(=O)− groups with any necessary rearrangement of double bonds.[87] para-Benzquinone (BQ) is a representative compound for this class of molecules. Quinones are capable of being reduced into the corresponding hydroquinone (HQ) and, reversely, the hydroquinone can be oxidized back to the quinone state, thus forming the BQ/HQ redox couple. The electrochemistry of BQ/HQ redox couples has been investigated for decades and it perhaps still remains one of the most thoroughly studied organic redox couples.[88] Quinones are not only cross conjugated ketones, the benzenoid structure that is one of their resonance structures brings aromatic character into these molecules.

5.2.1 Electrochemistry of Quinones

In general, there are three oxidation states involved in the quinone/hydroquinone redox process: the oxidized state (BQ), the intermediate oxidation state (semiquinone, SQ) and the fully reduced state (HQ). The electrochemistry of quinones heavily depends on the solvent and the electrolyte. In aqueous electrolyte with accessible protons, the redox reaction between BQ and HQ can be written as

\[ \text{BQ} + 2e^- + 2H^+ \rightleftharpoons \text{HQ} \]  

(17)

The reaction involves two electron transfer reactions and two proton transfer reactions. Possible pathways are presented in Figure 13. The dominating reaction path depends on the experimental conditions, such as the pH of the
electrolyte, as well as on the substituents on quinone.\textsuperscript{[88]} The SQ is unstable with respect to disproportionation in aqueous electrolyte at most pH values and only one redox peak is observed for this two electron redox reaction. As protons participate in the reaction, the formal potential of this redox reaction is depending on the pH of the electrolyte according to the Nernst equation as

\[
E^{0'} = E^0 + \frac{RT}{2F} \ln \left( \frac{[BQ][H^+]^2}{[HQ]} \right) = E^0 + \frac{RT}{F} \ln [H] = E^0 - pH \cdot 58 \text{ mV}
\]  

(18)

where \(E^{0'}\) is the formal potential, \(E^0\) is the standard potential and 58 mV is calculated for room temperature at 22 °C.

Figure 13. Redox cycles of 1,4-benzoquinone, including all proton and electron transfers. Horizontal series display the proton transfers and vertical series display the electron transfers. Oxidation states: BQ (benzoquinone), SQ (semiquinone) HQ (hydroquinone).

In aprotic electrolytes quinones are reduced in two successive one-electron steps in which BQ, BQ\(^{+}\) and BQ\(^{2-}\) are involved. Each redox step is observed as separate redox peak. Since BQ\(^{2-}\) is destabilized in aprotic solvent the redox potential for BQ\(^{2-}\) in aprotic electrolyte is much lower than for the HQ in aqueous electrolyte. For instance, in acetonitrile solution the formal potentials are 2.8 and 2.3 V vs Li/Li\(^+\) for the first and second reduction process respectively when tetra-n-butylammonium ion was used. (With lithium ion based electrolyte,\textsuperscript{[89]} the corresponding formal potential values are 2.75 and
2.6 V vs Li/Li$^+$ respectively\textsuperscript{[90]}, whilst 3.79 V vs Li/Li$^+$ in aqueous electrolyte (pH=0) was obtained.\textsuperscript{[91]}

5.2.2 Substituent effects

Substituent effects on the redox potential of BQ/HQ have been studied for decades.\textsuperscript{[92]} Great efforts have been made on developing proper computational methods in order to screen suitable quinone candidates for various applications.\textsuperscript{[93],[94]} By adding substituents on BQ or HQ the resonance structure may be altered, and the inductive effect introduced by the substituents also might affect the molecule.\textsuperscript{[88]} There are mainly two types of substituents, electron withdrawing groups (EWG) and electron donating groups (EDG). It is found, in general, that EWGs increases the formal potential of BQ/HQ whilst EDGs, on the contrary, would decrease the formal potential of BQ/HQ. The electronic effects from substituents can be evaluated from Hammett parameters which has been widely used as a tool to investigate the substituent effect on organic reactions as well as their mechanism.\textsuperscript{[95]} The large variety of possible structural modifications accessible through organic synthesis makes quinones especially attractive for the development of CRP-bases battery materials.

5.3 Quinone-pyrrole Dyad polymers (\textit{PaperVI})

In this thesis, the combination of HQ and PPy to compose poly-(hydroquinone pyrrole dyads) is based on the principle of ‘redox matching’ in order to obtain synergic effects between the CP and the PG. As shown in Figure 14, in aqueous electrolyte the formal potential of HQ in a range of pH from 0 to 7 fall within the conductive region of PPy. The quinone redox potential drops below the conductive region of PPy in aprotic electrolytes and hence this CP-PG combination is suitable for protic electrolytes only. In this thesis all synthesized polymers were hence characterized in aqueous electrolytes.
Figure 14. $E_0$ of HQ in aqueous electrolyte at various pH values (■) and in organic electrolyte where two peaks are observed and are independent with pH (× and +), the grey area indicates the general conductive region of PPy regardless of the electrolyte.

Attaching PG onto PPy could be achieved by substitution either on the nitrogen or the available β-carbon. Substitution on the nitrogen would be relatively easily achieved by nucleophilic substitution. However, it has been shown that substitution on the nitrogen greatly decreases the conductivity, even using small substituents such as a methyl group, due to twisting of the backbone induced by steric hindrance.\[96\] The steric effect from substitution on the β-carbon is considerably less, therefore substitution at this position is preferred. Moreover, with substituents on the β-carbon the polymerization is more likely to happen only at the α-carbon because there will be only one β-carbon available and the steric hindrance of substituents decreases the accessibility of the single available β-carbon, which will have a positive impact on the homogeneity of the polymer structure.\[97],[98]\]

5.3.1 Synthesis

In organic synthesis, Pd-catalyzed coupling reactions that employ various types of palladium complexes, provide effective methods to assemble two fragments via various linkages. The variety of reactions that can be catalyzed together with a large range of functional groups being tolerated, and usually high regio- and chemoselectivity, has resulted in their wide use in both industrial and academic laboratories.\[99\] In this thesis, Pd-catalyzed coupling reactions were employed extensively to synthesize the monomer dyads. To achieve regioselectivity for the β-position of pyrrole, the triisopropylsilyl (TIPS) group has been used as protection group.

The Suzuki-Miyaura cross-coupling reaction was employed to obtain dyads with hydroquinone directly linked to pyrrole. Using one equivalent of Na$_2$CO$_3$ instead of 2 equivalents as in the conventional procedure, the yield of product M1 could be increased. These reaction conditions were applied to
couple bromo-hydroquinone derivatives (1a-1h) with 3-boronic acid-1-(triisopropylsilyl) pyrrole (2). The isolated yield varied from 10% to 75% (Table 1).

Table 1. Preparation of 1,4-hydroquinone-1-(triisopropylsilyl)-1H-pyrrole derivatives

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<th>Entry</th>
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<th>Product</th>
<th>Yielda</th>
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<td></td>
<td></td>
<td>63</td>
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<tr>
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<td></td>
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<td>30</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>75</td>
</tr>
</tbody>
</table>

Ar-Br + B(OH)₂ + Na₂CO₃ (2M, 1eq) → MeOH/Toluene

Entry Ar-Br Product Yielda

1  \[
\text{Ar-Br} + \begin{array}{c}
\text{B(OH)₂} \\
\text{TIPS}
\end{array} \\
\text{MeOH/Toluene} \\
\text{Ar-TIPS}
\]

1a-1h 2 M1a-M1h
Isolated yield. Reaction conditions: bromo-hydroquinone derivatives (1 mmol) 1-(triisopropylsilyl) pyrrol-3-ylboronic acid (1.2 mmol), Pd(PPh₃)₄ (0.05 mmol), Na₂CO₃ (aq. 2M, 2 mL, 1 mmol), MeOH/toluene (1:1, 10 mL), microwave heating, 110 °C, 4 h.

During the synthesis, hydroquinone precursors with lower redox potential easily underwent oxidation, resulting in a product mixture containing a certain amount of bromo-para-benzoquinone (BQ). This hydroquinone oxidation is not desired for the Suzuki coupling reaction because the BQ might oxidize the active catalytic species Pd(0) to Pd(II) and the Pd(II) is hardly reduced back to Pd(0), which resulted in lower yields. To solve this issue a synthetic approach to couple bromo-para-benzoquinone derivatives (3a-3g) to pyrrole was developed and optimized (Table 2). As a result the desired products were obtained with decent yields varying from 20 % to 65%.

**Table 2** Preparation of para-benzoquinone-1-(triisopropyysilyl)-1H-pyrrole derivatives M2.
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<th>Yield&lt;sup&gt;a&lt;/sup&gt;</th>
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<td><img src="image14.png" alt="Chemical Structure" /></td>
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</table>

<sup>a</sup>Isolated yield together with desilylated product (yield is indicated in the racket). Reaction conditions: bromo-benzoquinone derivatives (1 mmol) 1-(triisopropylsilyl) pyrrol-3-ylboronic acid (1.2 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.1 mmol), Na$_2$CO$_3$ (aq. 2M, 2 mmol), dioxane (4 mL), 100 °C, 3 h
Deprotection of the pyrrole was performed by addition of 1 equivalent of TBAF in THF solution and the desired monomers, ready for polymerization, were obtained with overall yields varying between 20 % and 60 %. Desilylated compounds M1'a-M1'k were successfully polymerized. However, some of the resulting homo-polymers exhibited sluggish kinetics, probably due to steric hindrance caused by the functional groups on hydroquinone. This was particularly pronounced for polymers with bulky substituents on the quinone moiety. In order to reduce the effect of steric hindrance the monomers were copolymerized with unsubstituted pyrrole using the potential step method (Scheme 1).

Scheme 1. Synthesis of P1a-P1k, conditions: i) TBAF, THF, RT, 0.5 h; ii) copolymerizing monomers with pyrrole electrochemically via potential step method. (the number of monomers was given according to the sequence of the precursors)

5.3.2 Computational approach
DFT calculations were performed to predict the redox potential of the monomers. The Gibbs free energy at 298.15 K of each molecule was calculated as the sum of the energy in solution and the thermal correction of Gibbs free energy according to

$$
\Delta G_{\text{tot}}^0 = \Delta G_{\text{sol}}^0 + \Delta G_{\text{therm}}^0
$$

(19)

The standard potential of the reaction where hydroquinone (HQ) is oxidized to benzoquinone (BQ) as shown in eq.[17] can be calculated from the energies obtained according to

$$
\Delta G_{\text{ox}}^0 = \Delta G_{\text{tot(HQ)}}^0 - \Delta G_{\text{tot(BQ)}}^0 - 2\Delta G_{H^+(aq)}^0
$$

(20)

where the solvation energy in the standard state for $\Delta G_{H^+(aq)}^0$ is 1107.8 kJ/mol, and
\[ E^0 = -\frac{\Delta G^0_{\text{ox}}}{nF} \]  

(21)

Here \( n \) is the number of electrons transferred and \( F \) is the Faraday constant. The potential \( E^0 \) can be referenced to SHE, which has an absolute potential of 4.44 V at 298.15 K. \[^{[100]}\]

With a valid calculation method at hand, prediction of quinone redox potentials allows for better design of molecules. Good agreement between the predicted and experimental redox potentials was achieved, as indicated by the linear correlation between experimental and calculated data. In general, the redox potential increases with the electron-withdrawing effect of the substituents on quinone (Figure 15a). To assess the electron directing effect from the substituents the Hammett parameter \( \sigma_p \) was used and a clear correlation was found between the computed redox potentials and the sum of the Hammett parameter \( \sigma_p \) of the quinone substituents (Figure 15b).

Figure 15. a) Comparison of calculated and experimental redox potentials in aqueous solution at pH = 2.0 \((R^2 = 0.96)\); b) calculated redox potentials at pH = 2 for polymer P1a-P1k versus the sum of the Hammett parameter \( \sigma \) for all the substituents \((R^2 = 0.90)\).

5.3.3 Potential tuning

The CVs of the prepared copolymers in aqueous electrolyte at pH 2 are shown in Figure 16. In the CVs, the characteristic oxidative charging of the PPy backbone is observed for each polymer. The CVs nicely resembled CVs from PPy and quinone respectively, with well-preserved properties from these two subunits. As seen in Figure 16b, the redox potentials of the quinone-pyrrole dyads could be tuned within a 600 mV range by choice of quinone substituents.
5.3.4 Redox Matching

Redox matching in CRPs, meaning the redox potential of the pendant moiety being in the conducting region of the CP backbone, ensures fast charge transfer between the electrode and the PG. Conductivity of the CP backbone is a prerequisite for the well-functioning of redox PG. As shown in Figure 17a for P1a, reversible redox activity of the PG is retained upon altering the pH of the electrolyte from 0 to 6 as the formal potential of PG remains within the conducting region of the backbone. A decrease of 63 mV/pH of the formal potential was observed between pH 0 and pH 6, which is close to the theoretical value of 58 mV/pH for a 2H⁺, 2e⁻ reaction at 22°C (Figure 17b).
In contrast, with P1k, having the lowest redox potential in the series of CRPs presented above, the formal potential is close to the PPy onset doping potential already at acidic conditions. This CRP showed an especially sluggish quinone redox reaction with large peak split and irregular shape of the oxidative and reductive peaks. Increasing the pH of the electrolyte resulted in a downshift of the quinone formal potential (Figure 18a) and a decrease of 62 mV/pH was found (Figure 18b). In addition, increasing the pH of the surrounding electrolyte solution resulted in a decreased peak area and at pH=6.00 nearly no peak was observed. However, when the electrolyte was adjusted back to pH 2 after the series of measurements, the capacity was largely recovered, ruling out the possibility of polymer degradation during the measurements. Hence, we suggest that the loss of capacity can be attributed to the redox mismatch between the PG and CP. As the pH increases, the formal potential of PG shifts downwards and gradually drops out of the conductivity region of the CP backbone. As result, charges could not be transported sufficiently fast between the electrode and the PGs, resulting in a lower apparent capacity.
5.3.5 Prototype of quinone-pyrrole dyad polymers for full organic batteries

Full organic batteries may be constructed by employing two different CRPs in which the difference in formal potential between the PGs is adequately large. The adjustability of the quinone formal potential by substitution thus allows for the construction of quinone-CRP based batteries. By combining two quinone CRPs with different quinone formal potentials as cathode and anode respectively a cell potential as high as 500 mV could be achieved with the CRPs developed within this thesis.

As examples Figure 19b and 19e show the galvanostatic charge-discharge curves for two cells containing P1a or P1i as cathode and P1k as anode respectively. A plateau is observed during charging and discharging in both cases, which corresponds to the redox reaction of the PG of the electrodes. The derivative, dQ/dE, shows distinct peaks at 0.56 V for P1a/P1k and at 0.30 V for P1i/P1k (Figure 19c and 19f). The peak positions correspond well to the quinone formal potential difference between the two individual electrodes measured in a three electrode set-up (Figure 19a and 19d). The cells were cycled at very high rate with moderate performance and hence the charge transport properties of well-matched CRPs are sufficient to support high rates without addition of conductivity additives. To conclude, the agreement between the cell potential and the formal potential difference in individual electrodes, as well as the fast kinetics, proves the concept of using CRPs as battery materials and the possibility of constructing full polymer batteries using only quinone based CRPs.

Figure 19. a) CVs of P1k (in blue) and P1a (in red) in aqueous electrolyte buffered at pH 0; b) galvanostatic charge-discharge curves of P1a and P1k in a two-electrode set-up, a RE (Ag/AgCl) was used to monitor the potential change of the two electrodes over time. The cell potential, potential of P1a and potential of P1k against the RE is shown in black, red and blue respectively; c) differential capacity plot using the galvanostatic charge/discharge data to demonstrate the process in a voltammetric manner in which the formal potential is easily to read; d) CVs of P1k (in blue) and P1i (in orange) in aqueous electrolyte buffered at pH 0; e) galvanostatic charge-discharge curves of P1i and P1k in a two-electrode set-up with an exter-
nal RE (Ag/AgCl), the cell potential, potential of $P_{1i}$ and potential of $P_{1k}$ against the RE is shown in green, orange and blue respectively; f) differential capacity plot for a cell with $P_{1i}$ and $P_{1k}$.

5.4 Linker effects (Paper I–V)

In order to understand how the backbone-pendant interaction is affected by the linker a series of polymers with various linker units between the PPy backbone and the HQs were synthesized.

5.4.1 Synthesis

5.4.1.1 Poly-3-(2,5-hydroquinone)-1H-pyrrole

A Suzuki-Miyaura cross-coupling reaction was employed to obtain the dyads with directly linked HQ and pyrrole (compounds $M_3$ and $M_4$) following the synthetic routes in Schemes 2 and 3. Both 3-bromo-hydroquinone ($1a$) and 3-bromo-1,4-dimethoxybenzene ($4$) were coupled with 3-boronic acid-1-(triisopropylsilyl)pyrrole ($2$). It was found that the amount of base used in the coupling reaction is essential when 3-bromo-hydroquinone is used, and a reduced amount of base was employed in order to achieve a higher yield. The yields for 3-(2,5-dimethoxyphenyl)-1H-pyrrole ($M_3$) and 2-(1H-pyrrol-3-yl)-1,4-hydroquinone ($M_4$) after two steps are 47 % and 50 % respectively. The monomers were then polymerized by cyclic voltammetry.

![Scheme 2. Synthetic route for P2. Conditions: i) Pd(PPh$_3)_4$ (0.05 equiv.), Na$_2$CO$_3$ (2M, 2 equiv.), toluene/MeOH, microwave heating, 110 °C, 4h, 56 %; ii)TBAF (1.2 equiv.), THF, 0.5h, 83 %; iii) electrochemical polymerization via cyclic voltammetry; iv) BBr$_3$.](image-url)
Scheme 3. Synthetic route for P3. Conditions: i) Pd(PPh$_3$)$_4$ (0.05equiv.), Na$_2$CO$_3$ (2M, 0.8 equiv), toluene/MeOH, microwave heating, 110 °C, 4h, 72 %; ii) TBAF (1.2 equiv.), THF, 0.5h, 70 %; iii) electrochemical polymerization via cyclic voltammetry.

5.4.1.2 Poly-3-((2,5-hydroquinone)methyl)-1H-pyrrole

A Suzuki-Miyaura cross-coupling reaction was utilized again for synthesizing the target methylene linked compound 3-(2,5-dimethoxybenzyl)-1H-pyrrole (M5) as shown in Scheme 4. The synthesis started by preparation of 2,5-dimethoxy benzyl bromide from 2,5-dimethoxy benzyl alcohol with hydrogen bromide$^{[101]}$. Using typical conditions, the yield of the coupling reaction with 3-boronic acid-1-(trisopropylsilyl)pyrrole (2) was 56 %, which was considered satisfactory because of the ready availability of starting materials and the modest reaction time of 4 hours. The overall yield after three steps was 49 %. The corresponding polymer P4 was obtained by electrochemical polymerization via cyclic voltammetry.

Scheme 4. Synthetic route for P4, conditions: i) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2M aq.), MeOH/toluene, microwave heating, 110° C, 4h, 56%; ii) TBAF, THF, RT, 0.5h, 88%; iii) electrochemical polymerization via cyclic voltammetry; iv) BBr$_3$.

5.4.1.3 Poly-3-((2,5-hydroquinone)ethynyl)-1H-pyrrole

To synthesize the ethynyl linked dyad monomer, a Sonogashira coupling reaction was employed (Scheme 5). 2-Bromo-1,4-dimethoxybenzene (4) was converted to (2,5-dimethoxyphenyl)ethynyl)trimethylsilane (7), followed by desilylation with NaOH (aq.) to give 2-ethynyl-1,4-dimethoxybenzene
A second Sonogashira reaction of 8 with 3-iodo-1-(triisopropylsilyl)-1H-pyrrole afforded the protected pyrrole derivative 9. To avoid desilylation and homocoupling at high temperature, an overnight reaction at room temperature was performed, resulting in a yield for 9 of 50%. In summary, after a four step synthesis route, the total yield of M4 from 4 was 36%.

Scheme 5. Synthesis of P5, conditions: i) Ethynyltrimethylsilane, Pd(PPh3)2Cl2, CuI, PPh3, diethylamine, DMF, microwave heating, 120 °C, 15 min, 95%; ii) KOH (1 M, aq.), MeOH/CHCl3, RT, 0.5 h, 90%; iii) Pd(PPh3)2Cl2, CuI, triethylamine, 3-iodo-1-(triisopropylsilyl)-1H-pyrrole, THF, RT, 4 h, 50%; iv) TBAF, THF, RT, 0.5 h, 85%; v) electrochemical polymerization via cyclic voltammetry; vi) BBr3.

5.4.1.4 Poly-3-((2,5-hydroquinone)ethyl)-1H-pyrrole

The ethyl linked dyad monomer was synthesized by reducing 3-((2,5-dimethoxyphenyl)ethynyl)-1-(triisopropylsilyl)-pyrrole (9) which could be obtained as described for the synthesis of monomer M6 (Scheme 6). After five steps, starting from 2-bromo-1,4-dimethoxybenzene (4), compound M7 was obtained with 36% yield and was successfully polymerized electrochemically via cyclic voltammetry.
Scheme 6. Synthesis of P6, conditions: i) Pd/C, MeOH/acetone, RT, 1.5h, 98%; ii) TBAF, THF, RT, 0.5h, 85%; v) electrochemical polymerization via cyclic voltammetry; vi) BBr₃.

5.4.1.5 Poly-3-((2,5-hydroquinone)vinyl)-1H-pyrrole

After several failures of synthesizing a vinyl linker dyad monomer via Heck reaction, coupling 3-iodo-1-(triisopropylsilyl)-1H-pyrrole and dimethoxystyrene, the Wittig reaction was used to obtain the vinyl linker dyad 3-(2,5-dimethoxystyryl)-1H-pyrrole M8 as shown in Scheme 7. In this reaction, the phosphonium salt (11) was prepared in quantitative yield from 2,5-dimethoxy benzyl bromide, followed by deprotonation with t-BuOK to offer a dark red phosphorous ylide, to which 1-(triisopropylsilyl)-1H-pyrrole-3-carbaldehyde was added, followed by heating at 80 °C. The desired product (12) was obtained in 40 % yield after 3 h. After desilylation, monomers trans-M8 and cis-M8 were obtained and ready for polymerization. However, none of these monomers was possible to polymerize electrochemically under general conditions as a resistive layer was formed on the electrode which blocked further reactions.
Scheme 7. Synthetic route for 3-(2,5-dimethoxystyryl)-1H-pyrrole (M8), conditions: i) PPh$_3$, toluene, reflux, overnight, quantitative; ii) t-BuOK, THF, 0.5 h, not isolated; iii) 1-(triisopropylsilyl)-1H-pyrrole-3-carbaldehyde, 80°C, 3 h, 40%; iv) TBAF, THF, RT, 0.5 h, 86%; v) electrochemical polymerization via cyclic voltammetry (unsuccessful).

The vinyl linker monomer 3-(2,5-dimethoxystyryl)-1H-pyrrole (trans-M8 and cis-M8) failed to polymerize. DFT calculations on the oxidized species suggested that the spin density was delocalized over the entire molecule, thus possibly reducing the polymerizability at the α-carbons of pyrrole. DFT calculations indicated that the spin density mainly is localized on the α-carbons of pyrrole when a furan ring is used as linker, which should allow the polymerization to occur at the desired positions. To synthesize the monomer M9 with furan linker, the same strategy was adapted as for synthesizing compound M6 in Scheme 8. Compared to our previous studies, a different protecting group for the hydroquinone moiety was chosen, i.e. tetrahydropyranyl (THP) ethers rather than methoxy ethers, which allows the deprotection to proceed more readily and under milder conditions. The THP protecting group was removed under acidic condition with catalytic amounts of TFA, followed by removal of the TIPS protection group from pyrrole with a TBAF solution. Under acidic conditions, the hydroxyl group attacked the ethynyl triple bond, thus affording product M9 with an overall yield of around 30% after 5 steps. Monomer M9 was polymerized by cyclic voltammetry and the structure of the polymer was confirmed by solid state NMR.
Scheme 8. Synthetic route for P7, conditions: i) DHP, TFA, RT, overnight, 88%; ii) ethynyltrimethylsilane, Pd(PPh₃)Cl₂, CuI, PPh₃, diethylamine, DMF, microwave heating at 120°C, 1 h; iii) KOH (aq.), CHCl₃, MeOH, RT, 2 h, 72%; iv) Pd(PPh₃)₄, CuI, Et₃N, MeCN, 100°C, 3 h, 65%; v) a: p-toluenesulfonic acid monohydrate, DCM, MeOH, RT, 4 h; b: TBAF, THF, AcOH, RT, 48 h, 71%; vi) electrochemical polymerization via cyclic voltammetry.

5.4.2 Electrochemical characterization

For the series of monomers with various linkers cyclic voltammetry was employed to obtain the corresponding polymers. Taking P7 as an example, the polymerization of monomers shows an irreversible oxidation of pyrrole at around 0.4 V vs FeC⁰⁺ which results in the deposition of polymer on the GC disk electrode. Growth of polymer could be monitored by the increasing current at a lower potential at both oxidative and reductive scan which corresponds to the capacitive charging of the PPy backbone (Figure 20a). The resulting polymers were then characterized by cyclic voltammetry in aqueous electrolyte at pH 2 (Figure 20b). All polymers, P2 – P7, shared the same features, i.e. capacitive charge at lower potential which corresponds to the PPy backbone doping with an on-set potential at -0.2 – 0 V, and a reversible redox reaction at around 0.5 to 0.6 V vs SHE, assigned to the redox reaction of the pendant group (EQ⁰⁺). Identical EPPY and EQ⁰⁺ in P2 and P3 were observed, indicating that the deprotection reaction of the dimethoxy group with BBr₃ did not significantly affect the properties of the polymers. The variation of EQ⁰⁺ among the different polymers (Table 3) could be accounted for by the different linkers. The formal potentials of P4 and P6 are the same, which can be rationalized by the aliphatic nature of the linker. The conjugated linkers in the dyad based polymers exhibit a certain influence on the redox potential of PG with the triple-bond linker giving somewhat higher EQ⁰⁺ and
the double-bond linker somewhat lower $E_{Q_0}$. Surprisingly, the directly bonded polymers ($P_2$ and $P_3$) did not significantly alter the $E_{Q_0}$ despite the electron withdrawing nature of the pyrrole group.

![Figure 20. a) Electrochemical synthesis of $P_7$ from monomer $M_9$ by cyclic voltammetry; b) CV of polymer $P_7$ in aqueous electrolyte buffered at pH 2.00.](image)

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$E_{PPy}$ (V vs SHE)</th>
<th>$E_{Q_0}$ (V vs SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_2$</td>
<td>0.04</td>
<td>0.55</td>
</tr>
<tr>
<td>$P_3$</td>
<td>0.04</td>
<td>0.55</td>
</tr>
<tr>
<td>$P_4$</td>
<td>-0.19</td>
<td>0.52</td>
</tr>
<tr>
<td>$P_5$</td>
<td>-0.05</td>
<td>0.59</td>
</tr>
<tr>
<td>$P_6$</td>
<td>-0.03</td>
<td>0.52</td>
</tr>
<tr>
<td>$P_7$</td>
<td>0.08</td>
<td>0.54</td>
</tr>
</tbody>
</table>

5.4.3 Kinetics

The kinetics of charge transport is an important aspect when it comes to the development of high power EES materials. To assess the kinetics of the redox reaction in $P_7$ a scan rate dependency measurement was carried out. At low scan rates the peak split (potential difference between the oxidation and reduction peak potentials) for the PG redox reaction is small and nearly constant. At higher scan rates the peak potential increases and decreases linearly with $\ln(v/Vs^{-1})$ for the oxidation and reduction peak potential, respectively (Figure 21). Apparent rate constants ($k_{ox}^0$ and $k_{re}^0$ for the oxidation and reduction respectively) and transfer coefficients ($\alpha$) can be calculated assuming Laviron behavior as:[9]

Reduction:

$$E_{p,re} = E_{0r}^0 - \frac{RT}{azF} \ln \frac{azFv}{RTk_{re}^0}$$

(22)
Oxidation:

\[ E_{p,ox} = E^0' - \frac{RT}{(1 - \alpha)zF} \ln \left( \frac{(1 - \alpha)zF\nu}{RTk_{ox}^0} \right) \]  

(23)

where \( R \) is the universal gas constant, \( T \) is the temperature (295 K), \( F \) is the Faraday constant.

The linear fit of the peak potentials at high scan rates yields apparent rate constants for both the oxidation and the reduction process (Figure 21a). For the oxidation \( 1 - \alpha = 0.49 \) and \( k_{ox}^0 = 1.9 \text{ s}^{-1} \) and for the reduction \( \alpha = 0.79 \) and \( k_{red}^0 = 0.6 \text{ s}^{-1} \), taking \( E^0' = 0.54 \text{ V} \). This result is comparable to a similar quinone based CRP that we have investigated previously, where \( k_{ox}^0 = 4.4 \text{ s}^{-1} \) and \( k_{red}^0 = 0.6 \text{ s}^{-1} \) was found.\[102\]

For a non-diffusion limited process, the oxidation peak current \( (i_{p,ox}) \) is given by

\[ i_{p,ox} = \frac{z^2F^2}{4RT} \nu A\Gamma_{re}^* \]  

(24)

where \( A \) is the electrode area and \( \Gamma_{re}^* \) is the total surface coverage of the reduced species. In this expression \( i_{p,ox} \) is proportional to the scan rate \( \nu \) and thus \( \ln(i_{p,ox}) \) is a linear function of \( \ln(\nu) \) with a slope of 1. For a diffusion limited reaction, the \( i_{p,ox} \) is given by

\[ i_{p,ox} = 0.4463 \sqrt{\frac{F^3z^3D_R\nu}{RTAC_R^*}} \]  

(25)

where \( D_R \) is the diffusion coefficient and \( C_R^* \) is the bulk concentration of the reduced species. In this case \( \ln(i_{p,ox}) \) is a linear function of \( \ln(\nu) \) with a slope of 0.5. For \( \text{P7} \) a non-diffusion limited response was observed in which the logarithm of the quinone peak current \( (i_p) \) increases linearly with the logarithm of the scan rate \( (\nu) \) with a slope of 0.96 with \( R^2 = 0.97 \) (Figure 21b).

Figure 21. a) Peak potential for both oxidation and reduction at varying scan rates; b) oxidation peak current at varying scan rates for \( \text{P7} \) in aqueous electrolyte buffered at pH 2.
5.4.4 In situ Spectroscopy

ATR-FTIR was used to monitor the evolution of the absorption of the CPs as well as the PG during redox conversion in P7. As seen in Figure 22a, a strong band starting around 1700 cm\(^{-1}\) and extending to the visible region was observed in all spectra. This spectral feature is related to an electronic transition between the valence band and the doping-induced polaron or bipolaron in-gap states\(^{[103]}\) and matches well the doping process of the PPy backbone. A series of spectra were recorded upon potential reversal to verify the reversibility of the electrochemical process (Figure 22b). A comparison between spectra recorded during oxidation and during the corresponding reduction revealed that the position and intensity of the bands observed during oxidation and reduction are close to identical. Moreover, bands at 905, 976, 1059, 1121, 1246, 1437 and 1516 cm\(^{-1}\) grow with increased potential at the beginning of the oxidation. All these peaks have been observed in PPy and they originate from so-called doping-induced infrared active vibrations (IRAV), which are due to structural changes during the doping process. The band around 1634 cm\(^{-1}\) is assigned to the C=O stretching in BQ as this peak is also found in single molecule BQ. The intensity of this band starts to increase rapidly above 0.4 V, which is different from the IRAV bands induced by polymer doping.

![Figure 22. a) In situ ATR-FTIR spectra of P7 at different potentials with 100 mV interval; b) expanded region of the in situ ATR-FTIR spectra of the polymer during the oxidative process from 0.2 V to 0.7 V, using spectra at 0.2 V as background (upper part), and reductive process from 0.7 V to 0.2 V using spectra at 0.7 V as background (lower part). The numbers correspond to the wavenumbers of each absorbance band.](image)

5.4.5 Mass Change

The mass change (Δm) occurring during electrochemical redox conversion can be monitored using in situ EQCM. The counter-ions diffusing into or out of the polymer as well as the solvent expulsion and uptake account for these mass changes. The mass change of the P7 during CV measurements was monitored after initial equilibration at \(E= 0.1\) V vs SHE. Figure 23 shows the
mass change versus potential during the oxidative scan and the reductive scan together with the corresponding CV response. Starting from the polymer doping onset potential around 0.2 V vs SHE a monotonous mass increase is seen over the entire potential interval with no apparent difference in mass change during polymer doping (0.20–0.40 V vs SHE for oxidation) and the pendant group redox conversion (0.4–0.65 V vs SHE for oxidation). To further assess the mass change during the cycling, $\Delta m/\Delta n$ was evaluated, where $\Delta n$ is the charge change in moles as determined by integrating the CV. An average value of $\Delta m/\Delta n$ of 23 g/mol was found. This mass is significantly less than that of the predominantly available anion as dopant, NO$_3^-$, which has a molar mass of 62.00 g/mol. Therefore it is reasonable to suggest that the positive charges in the polymer backbone are charge balanced by both anion uptake and by cation expulsion. As the mass change is largely unaffected by the pendant group redox chemistry it seems likely that the polymer doping proceeds is unaffected by the pendant group redox chemistry.

![Figure 23. CV of P7 on EQCM electrode in aqueous electrolyte and the corresponding mass changes during the oxidative sweep and reductive sweep.](image)

5.4.6 Conductance

An in situ conductance measurement of P7 was performed by measuring the current passing through the polymer film in a bipotentiostat set-up using IDA electrodes with a potential bias of 10 mV between the two WEs. In the measurement the aqueous electrolyte was buffered at pH 0 and pH 2 and the results are shown in Figure 24. Under both conditions the conductance increases monotonously with the potential during the polymer doping process. For instance, at pH 2, the conductance started to increase at around 0.1 V vs SHE, which is in accordance with the onset doping potential as seen in the CV. The conductance increase during polymer doping is most evident at pH 0 where the conductance increases in the interval between 0.4 and 0.55 V. As HQ oxidation
starts, the conductance-increase with potential halts and reaches a maximum at 0.57 V vs SHE at pH 0 above which the conductance instead decreases over the entire HQ/BQ redox peak. It is evident from the conductance measurements at the different pH that the HQ/BQ redox reaction is responsible for the conductance drop.

![Figure 24. a) CVs of P7; b) in situ conductivity measurement of the polymer where a potential bias of 10 mV was applied between the WEs in aqueous electrolyte buffered at pH 0 and pH 2.](image)

Compared to P4, with a methyl linker, P7 is more conductive at the end of the redox process than P4 with a shorter linker which has almost no conductance at the end of the oxidation. The degree of conductance drop reveals the effect of the length of linker in CRPs regarding the interaction between the CP and the PG. A longer linker, as expected, weakens the interactions between the two. According to the observations in the EQCM as well as in the ATR-FTIR the doping process of the CP backbone is not significantly affected by the oxidation of the PG. Hence the drop in conductance cannot be accounted for a reduced number of charge carriers and must be attributed to a reduced charge carrier mobility. The decrease of charge carrier mobility would be rationalized by the twisting of backbone due to the enhance interactions between the PGs during the oxidation. This interaction would firstly be induced by the increase of hydrogen bonding between the newly formed BQ and not yet oxidized HQ, and secondly by strong π-π stacking among the PGs which is transmitted by the linker, eventually twisting the backbone. The packing induced force on the PGs should easily pass through the linker, and eventually affects the CP backbone due to the lacking of flexibility of the conjugated PG and CP structures. By observing a similar conductance drop in P4 which has an aliphatic linker, the possibility that the electronic interaction between CP and PG via a
conjugated linker leads to the conductance drop is ruled out. To solve this problem, a longer linker without any conjugation to the CP backbone would be an option. A more rigid CP backbone, such as PE-DOT,[104] would be more favorable because its aliphatic ring that is on the top of the conjugated polymeric backbone would relieve the forces induced by interactions between PGs.
6. Mechanism of charge transport in conducting redox polymers (Paper VII)

To study the mechanism of charge transfer in CRPs the conductance of P7 has been investigated. A temperature dependency study of conductance reveals that the charge transport occurs by thermally activated electron hopping in the polymer indicating that the material is best described as a Fermi glass.\[105\]. Moreover, by fitting the temperature dependence of conductivity to the Arrhenius equation the activation energy ($E_a$) may be accessed.\[106\]. Combined with in situ EPR spectroscopy the identity of the charge carrier is revealed and a mechanism for charge propagation is presented.

6.1 Temperature dependence of conductance

In the temperature dependent study of conductance the temperature was varied with increments in 10 degrees between 0°C and 40°C. The potential was swept between 0.2 V to 0.48 V vs SHE, i.e. above the polymer doping onset potential and below the potential on-set for oxidation of the PGs, and the conductance was monitored in situ by the use of IDA electrodes with 10 mV bias potential between the two WEs.

Using eq.[12] and eq.[16] the conductance can be expressed as

$$G = \mu n q A$$

In the hopping regime, the mobility can be expressed according to Arrhenius law as:\[105\]

$$\mu = \mu_\infty e^{-\frac{E_a}{kT}}$$

where $\mu_\infty$ is the mobility of charge carrier at infinite temperature.

By combining eq.[26] and eq.[27] the conductance can be expressed as

$$G = n q A \mu_\infty e^{-\frac{E_a}{kT}} = G_\infty e^{-\frac{E_a}{kT}}$$

\[28\]
by defining \( G_\infty = nq^2A\mu_\infty \), which is the conductance at infinite temperature. Applying the function (\( \ln \)) to both sides of the equation one obtains (here and in the following all quantities in logarithm are in SI units):

\[
\ln G = \ln G_\infty - \frac{E_a}{kT}
\]  

(29)

Figure 25. a) Plot of \( \ln G \) vs \( T^{-1} \) at potentials from 0.32 V to 0.48 V vs SHE with 10 mV increments, showing a clear temperature dependence of conductance; b) calculated activation energy \( E_a \) at varying potentials, including error bars.

As shown in Figure 25a, a linear decrease of \( \ln G \) with \( T^{-1} \) was found and linear fitting was achieved at each set of data with decent \( R^2 \) values (on average above 0.95) indicating that the temperature dependence of conductance adheres well to eq.[29]. Along with the fitting, the slope of each fitted line was obtained and the \( E_a \) at each potential was calculated accordingly (Figure 25b). An increase of \( E_a \) with increasing doping level was found, which is contradictory to the observed increase of conductance. However, the \( G_\infty \), as evaluated from the corresponding intercept of the fitting graphs, was found to increase with doping level, counteracting the effect of the increased \( E_a \) and this was found likely to be the dominating factor that accounts for the overall increase of conductance with potential.

6.2 Charge carriers

To further understand the origin of charge carriers a correlation between \( G_\infty \) and the charges (\( Q \)) withdrawn from the polymer was investigated. A plot of \( \ln G_\infty \) vs \( \ln Q \) is shown in Figure 26a, revealing a linear relationship with a slope of 2 (\( R^2=0.98 \)). This means that \( G_\infty \) is proportional to \( Q^2 \) indicating a second-order dependence of the conductance with respect to accumulated charge. In other words, this correlation implies that two charge carriers must encounter each other in the rate limiting process of charge transport. An \textit{in situ} EPR measurement of \textbf{P7} was performed to identify the charge carrier
species and the intensity of spins, which corresponds to the concentration of polarons, and was evaluated at various potentials. Plotting the intensity of spins as a function of charges reveals a linear relationship between these two parameters (Figure 26b), suggesting that polarons are the charge carrier species, as an equilibrium between polarons and bipolarons would be heavily dependent on the doping level with the polaron being favored at low doping levels and the bipolaron favored at high doping levels.

![Figure 26](image)

**Figure 26.** a) Plot of ln\(Q\) vs ln\(G_{\infty}\), in which \(q\) was calculated from CV and ln\(G_{\infty}\) was obtained from linear fitting in Figure 24. Linear fitting of this plot yields a slope of 2 with \(R^2 = 0.97\); b) intensity of spins vs. charges \((Q)\), a linear correlation is revealed by good fitting indicated by the straight red line with \(R^2 = 0.96\). The grey area indicates the measured potential region during *in situ* conductance measurement.

### 6.3 Model of charge transport mechanism

Based on the identification of the charge carrier species as polarons as well as the second-order dependence of the conductance with respect to injected charges, two plausible charge-transport mechanisms are proposed and shown in Figure 27. In the Figure, the polymers are separated into segments that could be either empty (the neutral state), polaron occupied or bipolaron occupied. Here, the bipolaron state is only transiently accessible during the transport but is unstable with respect to comproportionation to polarons. In mechanism A, two polarons generated on the same chain undergo a disproportionation reaction to form one bipolaron followed by electron transfer (ET) to a neutral site. The bipolaron then comproportionates into two polarons. In mechanism B, recombination between two polarons on neighboring chains leads to a net-transfer of one positive charge. After the transfer the formed bipolaron dissociates into two polarons. Both mechanisms agree with the second order dependence with respect to the number of charges as they rely on the collision of two charges and neither of them could be ruled out.
Nevertheless, mechanism A relies on the simultaneous transfer of two electrons which involves a reorganization given by the structural difference in between a neutral segment and a bipolaron segment and is therefore considered to be unlikely. Mechanism B, on the other hand, could benefit from having a distorted structure with a charge already in place on the electron donor site that would reduce the reorganization energies involved. An ET between a doubly charged segment and a neutral segment (ET in Mechanism A) would involve both the creation, on the electron donor site, and annihilation, on the electron acceptor site, of a charge distortion. The reorganization energy for ET from a distorted structure to another distorted structure (ET in Mechanism B) would be lower since this reaction only involves the annihilation of a charge defect (on the electron acceptor site). A similar reasoning for the first-order reaction, where the charge transport occurs between a charged polaron segment and a neutral segment, lead to the conclusion that also in this case higher ET reorganization energies are expected for this mechanism when compared to the polaron-polaron disproportionation reaction in Mechanism A. As a result the second order reaction might be favored over the first order reaction.

Figure 27. Illustration of two possible charge transport mechanisms in P7.
In this thesis, quinone pyrrole dyad polymers were designed and synthesized to investigate the suitability of this type of material, i.e. CRPs, as electrode materials in organic batteries. As an alternative to inorganic electrode materials, CRPs are more attractive in certain applications due to their safety, flexibility as well as simple disposal considerations. The use of CRPs solves dissolution issues which are generally found in small organic molecule based electrode materials. Moreover, the electronic conductivity obtained upon doping of the CP backbone eliminates the requirement of extra conductive additives to the device. Overall, the combined properties of CPs and PGs are achieved in the CRPs. By characterizing a series of quinone-pyrrole dyad polymers insight into the design principles of CRPs has been extended, including the interplay between the CP and PG properties, as well as the linker function and the charge transfer mechanism in these systems. More specifically, the achievements are as follows:

A series of quinone pyrrole dyad polymers with various substituents on the quinone units were synthesized. The formal potentials of quinone shift according to the electronic properties of the substituents, showing the adjustability of the formal potential of quinones in CRP systems. To access the capacitance from PGs the formal potential of PGs must be within the conducting region of the CPs, a condition referred to as redox matching in this thesis. Well-functioning battery cells were constructed by selecting two pairs of electrodes with a difference in quinone formal potential between the anode and cathode CRPs. The resulting cell potentials corresponded exactly to the difference in formal potential between the anode and the cathode CRP, exhibiting great potential of constructing a fully organic battery based on CRPs. However, the cell was operating in aqueous electrolyte which has several advantageous but also a limited potential window. Further work will continue exploring using CRPs in organic electrolytes in order to reach higher voltage output. Moreover, selecting proper EWG substituents for quinones to increase the formal potential of quinone based CRPs further would allow for increased cell voltages.

Furthermore, the choice of the linker between the CP and the PG affects the electrochemical properties of CRPs to a large extent. In the quinone pyrrole dyad polymer in which a vinyl linker was used, a conductivity drop upon the oxidation of the PG was observed even during the continuing doping of the CP backbone, suggesting that the strong interaction between qui-
none PGs induced a twisting of the backbone, leading to a low mobility of charge carriers. Future work will replace PPy with poly(3,4-ethylenedioxythiophene) (PEDOT) that is less prone to twisting. In the resulting polymer, a smaller influence from the PG onto the CP is expected.

In addition, in situ conductance measurement provided a feasible method to obtain the activation energy $E_a$ of charge transport in the bulk material by varying the temperature. In the studied polymer two possible pathways of charge transport including comproportionation/disproportionation of polarons were suggested. As a protocol of exploring the charge transport mechanism in CRPs by using various methods, combining in situ conductance measurement and EPR spectroscopy revealed the charge transport mechanism, which elucidates the correlation between structure and conductivity that is beneficial for further material development.

In conclusion, the concept of composing CRPs with quinone pyrrole dyads was investigated for their application as electrode materials for organic batteries. The adjustability in formal potential of quinones, and the fast charge transport achieved without requiring addition of conductive additives, makes this type of material particularly interesting for application as energy storage materials. To realize the goal of constructing a fully organic based battery, quinone based CRPs could be used as both cathode and anode material by suitable choice of quinone derivative. However, to achieve higher cell voltage, the combination of CRPs with n-doped character as anode material with a p-doped quinone based CRPs as the cathode material might be even more favorable.
8. Svensk Sammanfattning

Organiska batterimaterial föreslås som tänkbara alternativ för hållbara framtidiga material inom energilagring. Jämfört med oorganiska batterimaterial som används i stor utsträckning idag, har organiska batterimaterial oftast lägre vikt, säkrare hanterbarhet, och är mera miljövänliga vid såväl deras produktion som deras destruktion i slutet av livscykleln. Denna avhandling fokuserar på att utforska egenskaper och användningsmöjligheter av ledande organiska redoxpolymerer (CRPs) som består av en ledande polimerryggrad (CP) och en vidhängande grupp (PG) som kan genomgå en redoxreaktion. Dessa CRPs skulle kunna utgöra en ny typ av organisk elektrodmaterial. Ledande polymerer (CPs) har tidigare studerats som elektrodmaterial tack vare sin höga ledningsförmåga vid så kallad dopning, det vill säga oxidation eller reduktion. Dock har deras vanliga låga kapacitet varit i vägen för praktiska tillämpningar. Å andra sidan skulle organiska molekyler som kan ändra sitt oxidationstillstånd, så kallade redoxmolekyler, kunna vara attraktiva elektrodmaterial på grund av sin höga kapacitet. Dessvärr brukar hittills framtagna varianter av sådana molekyler uppvisa viss löslighet i batterielektrolyter, vilket ger dåliga prestanda vid upprepad laddning och urladdning, resulterandes i få battericykler, samt problem med självurladdning av batterierna. Genom att länka ihop dessa två enheter med kovalenta bindningar till en och samma molekyl (CRP) bör synergier av deras individuella egenskaperna vara möjliga, till exempel hög ledningsförmåga, hög kapacitet och justerbbara batteripotentialer. Dessutom bör dessa polymermaterial ha avsevärt lägre löslighet i batterielektrolyter. I denna avhandling undersöks en serie av ledande kinon-pyrrol dyadpolymerer (CRPs) i vilken polypyrrol användes som den ledande polymeren (CP) och kinoner som vidhängande redoxaktiv grupp (PG) (Figur I).

För det andra har effekterna av länken mellan CP och PG undersökts. I en grundlig studie på en kinon-pyrrol dyadpolymer med en vinyllänk har olika in situ metoder tillämpats. Därvid konstaterades att polymeren (CRP) dopas kontinuerligt medan dess ledningsförmåga började minska med tilltagande laddning av PG, och att tilltagande oxidation av PG går hand i hand med minskad ledningsförmåga. En tänkbar förklaring på molekylär nivå är att oxidationen av PG till kinonformen resulterar i en ökad andel av vätebinding mellan den nybildade kinonen och ännu ooxiderad PG i hydrokinonform. Dessa vätebindingar ändrar packningsgraden av PGs, vilket resulterar i vridning av polymericryggraden och därmed minskad rörlighet hos laddningsbärare trots fortsatt dopning.

För det tredje har mekanismen bakom laddningstransporten i CRPs undersöks. Genom att mäta ledningsförmågan in situ vid varierande temperaturer kunde ett samband mellan ledningsförmåga, antalet laddningar som passerar genom polymeren och temperaturen detaljstuderas. Via en Arrheniususekvation kunde aktiveringsenergin för laddningstransporten bestämmas. En andra ordningens reaktion föreslås, baserad på korrelationen mellan antalet laddningar och laddningsbärarnas densitet. Genom en in situ EPR-studie
där antalet spins ökar linjärt med polymerens dopning, har polaroner, dvs katjonradikaldefekter, föreslagits som laddningsbärare. Som två möjliga vägar för laddningstransport har disproportion av polaroner och komproportion av bipolaroner, dvs dubbelt positivt laddade defekter, identifierats. Denna studie belyser inte bara processen för laddningenstransporten i denna typ av material utan beskriver även en metod för att undersöka laddningstransporten i organiska polymerer.
I would like to thank everyone who has helped and supported me in the past years.

First of all, I would like to thank my main supervisor, prof. Martin Sjödin. Thanks for your patience and encouragements. I really enjoyed your passion towards research, also I enjoyed the conversation with you about politics, food etc. I really liked the literature meeting from which I did learn a lot, and enjoyed the discussion a lot.

My supervisor Prof. Adolf Gogoll. I really don’t know how to simply express my gratitude to you, as I always felt blessed since you became my supervisor both in my master and PhD study. From the first NMR course to later on studies, you taught me a lot of things that not only matters to my research but also to my life. Every time when I was down, you could always find a way to get me out.

My supervisor Prof. Maria Stromme, thank you for the encouragement and support during the past years, always felt inspired by your enthusiasm in sciences.

Prof. Henela Grennberg, thank you for having nice discussions during the group meeting, thanks for the comforts as well as encouragement that you gave when it comes to dark time. Prof. Leif Nyholm, thank you for teaching me electrochemistry, it was a very enjoyable course.

Dr. Christoffer Karlsson. Thank you for being my project partner as well as travel companion for so many years. I learned a lot from you, and it was enjoyable to travel with you. Also thanks for showing Swedish culture to me.

I would like to thank my project members: Xiao Huang, thanks for all the good time we had together, also nice discussions on the project. Mia Sterby and Lisa Åkerlund, thank you for being pleasant companies in the project as well as in the conferences in which we had really great time. Dr. Rikard Emanuelsson, thank you for nice collaborations and good discussion about the project. Christian Strietzel, it is nice to discuss politics with you, maybe you could be the next ‘Angela Merkel’. I also would like to thank other project members for nice discussions: Dr. Henrik Olsson, Dr. Petter Tammela, Dr. Li Yang, Huan Wang and Dr. Stéven Renault.

I would like to thank all other past and present members of the NFM group, especially to Dr. Teresa Zardán Gómez de la Torre, what a wonderful office roomie you are, all I wished was the wall would be a bit thicker so that our laughter won’t cross to our neighbors while we were having great fun on
talking about sorts of things. Dr. Sara Frykstrand, thank you for bringing contagious positive energy to surroundings. Igor Rocha, for showing me South American dishes. Dr. Jonas Lindh for sharing gossip about BMC, Dr. Daniel Carlsson for offering nice SEM pictures of the polymers. Simon Gustafsson, thanks for making coffee in the morning, nice debate during lunch time, and your efforts to keep kitchen clean. Maria Vall, it was quite nice to meet you on the bus to work every time, it was quite fun to talk with you, good start for the day. All Chinese members in the group: Changing Ruan, Rui Sun, Kai Hua, Peng Zhang, Chao Xu, JiaoJiao Yang, thanks for sharing good food and experiences.

I also would like to thank my colleagues at BMC, Michael Nordlund and Sandra Olsson, thanks for all the time that we spent together. I really enjoyed the time of being in the lab with you, the fika and the games also the New Year eves etc., a lot of good memories, I hope it would continue. Anna Lundstedt, thank you for the nice conversations about graduation as well as sharing person feeling about sorts of things, it is always nice to have fika with you. Dr. Magnus Blom, thank you for showing me the peptide-synthesis which made me a ‘peptide-boy’, hopefully I am not the last one. Dr Sara Norrehed, thanks for sharing your great knowledge about NMR, especially some nice tips and tricks. Jiajie Yan and Jie Yang, thanks for being nice lunch companions. Dániel Kovács, thanks for sharing your stories as well as Hungarian food. Jiafei Poon, thank you for being a nice flat-mate and a nice person to discuss chemistry.

Besides, I would like to express my gratitude to the following people:

Dr. Julien Andres, thank you for being such a wonderful flat-mate, sharing good food as well as your good taste of wines, whiskeys and movies. Thanks for reviewing my papers and thesis.

Dr. Tao Yang, it is great pleasure to know you. Thanks for sharing life experiences and wisdom with me. It is hard to find a person that understands me so well.

The brotherhood that I enjoyed, Zhenggang Yu, Kelvin Tang, Siuhin Pang, Saam-Ove Ruste and all the members in ‘Shuangsheng’ boardgame team: Dr. Xu Cheng (the Captain), Beichen Xie, Mingyu Yang, Fangming Lan, Wanjun Chu, Huimin Zhang, Da Zhang, Yu Liu, thanks for your companion in the past years, almost feel like we are a big family and you have made my life in Sweden became much brighter and happier.

最后，我想感谢我的父母。感谢你们在这多年来对我的爱与宽容，感谢你们对我无条件的付出与支持。因为有你们，我的一切才有了可能，这一切的可能正是我如此享受我生命的原因，谢谢你们！
10. References


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