On the Surface of Conducting Polymers

Electrochemical Switching of Color and Wettability in Conjugated Polymer Devices

Joakim Isaksson
“It's a one-day experiment...

...OK, OK, maybe two days...”

Professor Magnus Berggren
ABSTRACT

Since the discovery in 1977 that conjugated polymers can be doped to achieve almost metallic electronic conduction, the research field of conducting polymers has escalated, with applications such as light emitting diodes, solar cells, thin film transistors, electrochemical transistors, logic circuits and sensors. The materials can be chemically modified during their synthesis in order to tailor the desired mechanical, electronic and optical properties of the final product. Polymers are also generally possible to process from solution, and regular roll-to-roll printing techniques can therefore be used for manufacturing of electronic components on flexible substrates like plastic or paper. On top of that, the nature of conjugated polymers enables the creation of devices with novel properties, which are not possible to achieve by using inorganic materials such as silicon.

The work presented in this thesis mainly focuses on devices that utilize two rather unique properties of conducting polymers. Conducting polymers are generally electrochromic, i.e. they change color upon electrochemical oxidation or reduction, and can therefore be used as both conductor and pixel element in simple organic displays. As a result of the electrochemical reaction, some polymers also alter their surface properties and have proven to be suitable materials for organic electronic wettability switches. Control of surface wettability has applications in such diverse areas as printing techniques, micro-fluidics and biomaterials.

The aim of the thesis is to briefly describe the physical and chemical background of the materials used in organic electronic devices. Topics include molecular properties and doping of conjugated polymers, electrochromism, surface tension etc. This slightly theoretical part is followed by a more detailed explanation of device design, functionality and characterization. Finally, a glance into future projects will also be presented.
ACKNOWLEDGEMENTS

This licentiate thesis is hopefully a step on the way towards my final Ph. D. but even though I am only half way there, I could not have come this far on my own. I would therefore like to take this opportunity to express my sincerest thanks to the following people:

**Magnus**, my award-winning professor, for giving me the opportunity to work in a constantly evolving field of science and for always being a source of inspiration.

**Nate**, my electrochemistry supervisor and science reality-check, for always taking the time to help, whatever the problem or question may be.

**Xavier**, the molecular physics wiz, for valuable comments on my manuscript.

**Payman**, my lab partner on the display color project, for many lab-hours with the endless number of WM solutions

**David**, my Ph. D. hero and BioX “sidekick”, for taking some of my workload when I have focused on writing this thesis.

**Sophie**, the woman who seems to know and fix anything slightly related to administration, for knowing and fixing everything

The entire group of **Organic Electronics** (at this date consisting of Magnus, Nate, Xavier, Sophie, David, Peter, Payman, PeO, Elias, Fredrik, Lars, Linda, Emilien and Oscar) for great scientific team-spirit and personal friendship.

**The co-authors on my manuscripts.** Special thanks to **Calle**, the XPS perfectionist, for doing the messy XPS measurements on the wettability switch.

The people at **Acreo** for help in the lab, with patenting etc.

And finally on a more personal level...

**My family**, especially:

**Johanna**, my lovely wife and best friend, for everything (unspecified) and specifically for great support at home during times when I have worked a lot. You always believe in me.

**Moa**, my beautiful and lively daughter, simply for existing and for teaching me the value of time management (the hard way).

Joakim Isaksson, Norrköping, September 2005
LIST OF INCLUDED PAPERS

Paper 1

A Solid-state Organic Electronic Wettability Switch
Joakim Isaksson, Carl Tengstedt, Mats Fahlman, Nathaniel D. Robinson and Magnus Berggren

Contribution: All experimental work, except photoelectron spectroscopy. Wrote the first draft of the manuscript and was involved in the final editing and submission of the manuscript in cooperation with the co-authors.

Paper 2

Electronic Modulation of an Electrochemically Induced Wettability Gradient to Control Water Movement on a Polyaniline Surface
Joakim Isaksson, Nathaniel D. Robinson and Magnus Berggren
Submitted to Thin Solid Films

Contribution: All experimental work. Wrote most of the manuscript and coordinated the final editing and submission of the manuscript in cooperation with the co-authors.

Paper 3

On Design Criteria for Active Materials in Printable Electrochromic Polymer Displays.
Payman Tehrani, Joakim Isaksson, Wendimagegn Mammo, Mats R. Andersson, Nathaniel D. Robinson and Magnus Berggren
Submitted to Thin Solid Films

Contribution: About half of the experimental work (not including polymer synthesis). Was involved in the final editing of the manuscript in cooperation with the co-authors
## CONTENTS

1. **INTRODUCTION**  
   
2. **CONDUCTING POLYMERS**  
   2.1 Conjugated polymers  
   2.2 Doping of conjugated polymers  
   2.3 Optical properties of conjugated polymers  
   2.3.1 Absorption and emission  
   2.3.2 Electrochromism in conjugated polymers  
   2.4 Examples of commonly used conjugated polymers  
   2.4.1 Polythiophenes  
   2.4.2 PEDOT:PSS  
   2.4.3 Polyaniline  

3. **SURFACE ENERGY – WETTABILITY**  
   3.1 Surface tension in theory  
   3.2 Contact angle measurements  
   3.3 Other techniques to study surface tension  
   3.3.1 Pendant drop  
   3.3.2 Tensiometry  

4. **ELECTROCHEMICAL DEVICES**  
   4.1 Reduction and oxidation of conducting polymers  
   4.2 “Structure 1”  
   4.3 “Structure 2”  
   4.4 “Structure 3”  
   4.5 Electrochemical wettability switch  
   4.6 Electronic modulation of wettability gradients  
   4.7 PEDOT:PSS displays with improved optical contrast  

5. **ONGOING AND FUTURE WORK**  
   5.1 BioX  
   5.2 Wettability switch  

REFERENCES  

PAPER 1  

PAPER 2  

PAPER 3
1. INTRODUCTION

In the year 2000, the Nobel Prize in chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for “the discovery and development of electrically conductive polymers”\(^1\). 23 years earlier, these three gentlemen had discovered that polymers (what we generally call plastics) could not only be used as insulating materials but also be made electronically conducting.\(^2\) Until their surprising breakthrough, polymers were considered as important materials because they are easy to process from solution and their mechanical properties can be tailor-made during synthesis, but intrinsically conducting polymers sounded like something of a paradox. Some polymers were already known to have semiconducting properties but Heeger, MacDiarmid and Shirakawa found that the materials can be “doped” to achieve metallic conduction.

The idea of making electronic devices with the same process, flexibility and, perhaps more importantly, at the same cost as e.g. a plastic bag is of course very appealing and the discovery has opened up a completely new field of science. Since the polymers have a carbon base, much like the materials in nature, the use of intrinsically conducting polymers in electronic devices is often called organic electronics.

Because it is generally possible to dissolve or emulsify polymers in organic solvents and thereby handle the materials as liquids, regular printing techniques can be used for manufacturing of electronic components.\(^3\)-\(^5\) Instead of printing different colors, several conducting polymers can be used as inks in the printing
Introduction

press. There are of course a number of practical issues to deal with but in principle roll-to-roll printing of electronics on flexible substrates such as paper or insulating plastic foil is already a reality. The speed and performance of such printed devices is not comparable to what is manufactured in the traditional silicon industry but since a printing press can process several 100 meters per minute, the cost for each device is close to nothing. This, in combination with the environmental hazards of tedious silicon processing and the fact that many conducting polymers are biocompatible makes organic electronics even more interesting.

Apart from the electronic conductivity itself, conducting polymers have a number of other exceptional properties (compared to inorganic materials) that makes it possible to create completely new types of devices. Examples of organic electronic applications are light emitting diodes,\textsuperscript{6-8} solar cells,\textsuperscript{9-11} thin film transistors,\textsuperscript{12,13} electrochemical transistors and logic circuits\textsuperscript{14-16} and sensors.\textsuperscript{17}

The work in this thesis mainly focuses on devices that utilize two specific properties of conducting polymers. First, conducting polymers change color upon electrochemical oxidation or reduction and can therefore be used in simple display pixels. Second, as they change color, some polymers also alter their surface properties and have proven to be suitable materials for organic electronic wettability switches, with applications in areas such as printing techniques, micro-fluidics and biomaterials. The aim of the thesis is to briefly describe the physical and chemical background behind the organic devices, followed by a more detailed explanation of device functionality and characterization. Finally, a glance into future projects will also be presented.
2. CONDUCTING POLYMERS

A polymer (poly = many in Greek) is a material that consists of many repeated units, called monomers (mono = one). Natural polymers are for instance DNA, proteins, cellulose etc., but polymeric materials can also be synthesized. Since the number of possible polymer designs is close to infinite, the chemical and physical properties can more or less be tailor-made for each application. Most polymers or their monomers are soluble in organic solvents. This means that the material can be handled and processed as a liquid and therefore simple manufacturing techniques such as moulding, casting, spin coating, screen printing etc. can be used to create structures and shapes before or after polymerisation. The class of polymers that can conduct electricity is called conducting polymers.

2.1 Conjugated polymers

What is the difference between the polymer in a plastic bag and one that can conduct electricity like metals? A common material in regular plastic bags is polyethylene, which is a very good insulator. In polyethylene, each carbon binds to two other carbons and to two hydrogen atoms (Figure 1a). The physical chemist would say that the carbon is sp\(^3\)-hybridized (hybridization between the s-, p\(_x\), p\(_y\) and p\(_z\)-orbitals yields four equal hybrid orbitals) and forms four σ(sigma)-bonds to the surrounding atoms. Every carbon valence electron is then localized in such a bonding molecular orbital and can therefore not transport current.
Polyacetylene (Figure 1b) has a very similar chemical structure but in this case each carbon only binds to three other atoms. The carbon is now sp$^2$-hybridized and forms three $\sigma$-bonds. However, since carbon has four valence electrons, each carbon atom has one electron left in a non-hybridized $p$-orbital. These atomic $p$-orbitals overlap, perpendicular to the polymer backbone, between neighboring carbon atoms to form molecular $\pi$(pi)-orbitals. The result is a conjugated molecular structure with alternating single and double bonds between carbon atoms.

The most stable form of polyacetylene (trans-polyacetylene), drawn with shorthand notation (each vertex represents a carbon atom with hydrogen atoms) in Figure 2, has a so-called degenerate ground state, i.e. there is no difference in energy if the positions of the double bonds and the single bonds are interchanged. This means that the electrons in the $\pi$-bonds can be found between any two carbon atoms and thus move along the polymer chain. The longer the molecule, the smaller the distance between energy levels and for “infinitely” long molecules energy bands are formed.

If all bond lengths between carbon atoms were the same, polyacetylene would behave like a one-dimensional metal. This is not the case, because of so-called Peierls distortion, i.e. it is more energetically favorable for the molecule to have an alternating bond configuration. Therefore, an energy gap appears in the band

---

**Figure 1.** Chemical structures of a. Polyethylene and b. Polyacetylene with shorthand notations below.
structure, like for inorganic semiconductors. The highest occupied molecular orbital (HOMO) defines the top of the valence band for an infinitely long molecule, and the lowest unoccupied molecular orbital (LUMO) is the bottom of the conduction band.

Figure 2. Polyacetylene has a degenerate ground state, i.e. the two single-double bond alternation schemes have the same total energy.

The presence of a band gap means that energy has to be put into the system in order to get electrons from the valence band to the conduction band and pure polyacetylene therefore has semiconducting properties instead of metal behavior. Due to the conjugation (delocalization of $\pi$-electrons), the bandgap is still very small (1.5 eV) compared to polyethylene (>8 eV), which is an insulator.

Most other conjugated polymers (e.g. polythiophene, see 2.4.1) have a non-degenerate structure, i.e. there is only one energy ground state. In this case the single and double bonds cannot be interchanged without a cost in energy (distortion of the molecular structure) and the band gap is slightly larger than in a degenerate conjugated molecule. Once again, thanks to the conjugation, the band gap is small enough to yield semiconducting properties.

2.2 Doping of conjugated polymers

Pure polyacetylene is a semiconducting material, but although the conductivity is higher than in polyethylene, it is far from that of a metal. Heeger, MacDiarmid and Shirakawa discovered that charge carriers can be introduced in polyacetylene by doping the material, which results in a conductivity increase
by several orders of magnitude. This discovery earned them the Nobel Prize in chemistry and revolutionized the research field of conjugated polymers. A comparison of conductivities for different organic and inorganic materials is shown in Figure 3 (from ref. 18).

Positive doping of a conjugated polymer means that an electron is removed from the valence band (addition of a positively charged “hole”) and negative doping is when an electron is added to the conduction band. Although the physics is different, this way to create mobile charge carriers in an organic semiconductor can be compared to p- and n-doping, respectively, in inorganic semiconductors (like Si). However, a high percentage of dopant is needed to increase the conductivity in the polymer compared to only a few ppm in Si. Conjugated polymers can be doped in a number of different ways, such as chemical and electrochemical doping, charge injection doping, photo doping and acid-base doping.18,19

![Figure 3](image-url)

**Figure 3.** Conductivity of a few organic and inorganic materials. Adapted from ref. 18
For degenerate systems, like *trans*-polyacetylene, a geometrical defect in the polymer chain can create a modification of the bond length alternation pattern, as shown in Figure 4. The domain “wall” between the two types of bond length alternation is called a soliton and is characterized by a new energy state in the middle of the band gap. The “extra” charge resides in this state, which is localized over a relatively short distance ($X = 10$ to $20$ C-C bonds in Figure 4). If the bond order is shifted without the addition of an external charge, a neutral soliton with spin $= \frac{1}{2}$ is created, as shown in Figure 4a. Solitons are present in *trans*-polyacetylene because of defects or simply on chains containing an odd number of carbon atoms. Although they have no charge, the solitons can be detected experimentally because of their spin.

*Figure 4.* Solitons in *trans*-polyacetylene. **a.** Neutral. **b.** Negative. **c.** Positive. $X$ denotes the localization of the soliton.
When an electron is added to the polymer chain through n-doping, existing solitons are energetically favorable to charge and a negative soliton with no spin appears (Figure 4b). If an electron is instead subtracted from the polymer, a positive soliton without spin is created as seen in Figure 4c.\textsuperscript{20,21} The energy states described above refer to the idealized case of an isolated polymer chain. In reality, interactions between chains has to be considered and if the charged states stem from chemical or electrochemical doping, a counter ion will be ionically coupled to the polymer chain in order to maintain charge neutrality (see also 4.1).

Most conjugated polymers are, however, not degenerate, i.e. they have one unique energy ground state. When a non-degenerate conjugated polymer is doped, the geometric distortion induces a state of higher energy. The structure distortion coupled to the introduced charge is called a polaron, which can move along the polymer chain and thereby participate in the electronic conductivity of the material.\textsuperscript{22,23} Polarons can actually also be created in non-degenerate systems, such as trans-polyacetylene, but only at higher doping levels when all solitons have been charged.

One example of a simple non-degenerate conjugated polymer is poly(paraphenylvinylene) (PPV). Doping of the polymer changes the bond alternation and creates a region with quinoid structure instead of the regular aromatic, as shown in Figure 5. This also leads to the appearance of new energy levels inside the band gap. Upon further doping, it is sometimes energetically favorable to form one bipolaron, which is doubly charged and spinless, instead of two separate polarons. In a simplified picture, the charges in the bipolaron repel each other because of Coulomb forces but, at the same time, the separation of two polarons cost elastic energy since the quinoid configuration is a higher energy state than the aromatic. This situation can be compared to the equilibrium state of a spring and the bipolaron will therefore be localized over a few rings, as shown in Figure 5.
The energy levels of the polarons and bipolaron are related to the HOMO and LUMO of the quinoid form and the energy difference between these levels is smaller than in the aromatic case. The new levels formed inside the bandgap upon doping create new allowed optical transitions at lower energies (see also 2.3). As in the soliton case, the formation of polarons and bipolarons described above is idealized and correspond to one isolated molecular chain without charge neutralizing counter ions.

Figure 5. Formation of a negative polaron and bipolaron in poly(para-phenylvinylene).
2.3 Optical properties of conjugated polymers

Conjugated polymers have small optical bandgaps and many of the materials therefore absorb light in the visible region (wavelengths, $\lambda = 400$-$800$ nm; or energy, $E = 1.5$-$3$ eV). Consequently, conducting polymers are often colorful materials, but this also means that if the electronic structure and allowed optical transitions is modified, e.g. upon doping, we can follow the color transition with our eyes when the absorption of light changes.

2.3.1 Absorption and emission

A material can absorb a photon (a quantum of light) if the photon energy matches the difference between the energy of the excited state and the ground state (Figure 6). If that is the case, the molecule receives the photon energy and is excited to a higher energy state. A molecule in this excited state goes back to a lower energy state via radiative or non-radiative processes. In a radiative decay, a new photon is created and light is thereby emitted (spontaneous emission). The light emission is quenched if a non-radiative decay allows the molecule to come back to the ground state by donating the excitation energy to surrounding molecules via collisions or energy transfer. Since some of the energy is always lost in vibrations, the energy of the emitted light is lower than the absorbed light (red-shifted wavelength), as shown schematically in Figure 6.

Organic light emitting diodes also utilize the radiative decay of an excited state to emit light, but in this case, excited electron-hole pairs (referred to as excitons) are created by injection of charges with an applied electric field. Organic solar cells work the other way around. Incoming photons excite the molecules and, when the excited charges are separated, power can be collected at the electrodes.
Figure 6. Absorption and emission. **a.** Schematic energy diagram showing two electronic states with vibrational levels. The incoming photon is absorbed by the molecule, which is then excited. After vibrational relaxation, the molecule can go back to the electronic ground state by emission of a new photon with lower energy. **b.** Sketch of absorption and emission spectrum with visible vibrational peaks. The emitted light has a lower energy and the wavelength is thereby higher (red-shifted).
2.3.2 Electrochromism in conjugated polymers

Since optical absorption corresponds to differences in energy states, the absorbance spectrum of a material is a signature of the electronic and vibrational levels (Figure 6). When a conjugated polymer is doped, new energy levels are created inside the band gap (as seen in Figure 5) and new optical transitions are thereby possible. Many conjugated polymers can be electrochemically doped, with a resulting change not only in conductivity but also in color. Such a material, which alters color upon electrochemical switching, is called electrochromic.\textsuperscript{24-26} Examples of applications for organic electrochromic materials are flexible thin electrochemical displays,\textsuperscript{14} autodimming windows\textsuperscript{27} etc.

The use of organic materials for electrochromic applications has several advantages. The possibility to process the materials from solution makes large area, roll-to-roll manufacturing on flexible substrates realizable. Addition of side chains to conjugated polymers or modification of the molecular chain length alters the energy level configuration and thereby the color of the material.\textsuperscript{28,29} It is therefore possible, to some extent, to design materials with exactly the right properties to match the demand of a specific application. Since conjugated polymers can also be electronically conducting or semi-conducting, organic electrochromic displays may be integrated with electrochemical transistors\textsuperscript{15} and logic\textsuperscript{16} to build truly all-organic opto-electronics.\textsuperscript{14} Examples of common electrochromic polymers are given below and simple organic electrochemical devices are described in more detail in 4.2-4.4.

2.4 Examples of commonly used conjugated polymers

The research field of conjugated polymers has accelerated rapidly since the discovery of doped polyacetylene, and a number of different polymers and their derivatives have been synthesized in order to achieve materials with specific properties. Polyacetylene itself is of course the "original" conducting polymer but difficulties with processing and poor stability in ambient atmosphere limits
the use of the material in real applications. Other groups of polymers are therefore today utilized much more frequently in organic electronics. A few materials interesting for the work in this thesis will be presented below.

### 2.4.1 Polythiophenes

Polythiophene and derivatives thereof have become popular conjugated polymers for applications such as light emitting diodes, field-effect transistors, solar cells, memory applications and capacitors. The first synthesis of a material similar to polythiophene was reported already at the end of the 19th century but it was not until the 1980s that the defined conjugated polymer was presented.

![Figure 7. a. polythiophene. b. poly(3-alkylthiophene), R denotes an alkyl chain. c. Example of the regioregular configuration, which preserves the conjugation in the material.](image)

Polythiophenes (Figure 7a) are insoluble in organic solvents due to the rigid polymer backbone and side-chains have therefore been added to the material. Common polythiophene derivatives are molecules with an alkyl chain on the 3-position of the thiophene ring as shown in Figure 7b. Poly(3-hexylthiophene) (six carbons in the alkyl side chain) has proven to be a material with both good solubility in organic solvents and nice film-forming properties. Today, pure and highly regioregular head-to-tail poly(alkylthiophenes) (Figure 7c) are commercially available and can be used to create conjugated and well ordered...
Conducting Polymers

Conducting thin layers by e.g. spin casting. Poly(3-hexylthiophene) is one of the active materials in the electrochemical wettability switch, described in 4.5 and Paper 1.

2.4.2 PEDOT:PSS

One polythiophene derivative has become especially important in organic electronics, particularly for electrochemical devices. During the late 1980s, Bayer AG in Germany developed poly(3,4-ethylenedioxythiophene) or PEDOT (Figure 8a). This p-doped polymer in combination with the charge balancing counter-ion poly(styrenesulfonate) (PSS⁻) (Figure 8b) forms a water soluble (emulsion) polyelectrolyte system (PEDOT:PSS) with nice film-forming properties, high conductivity and tremendous stability in the p-doped (oxidized) state.28 Applications incorporating PEDOT:PSS range from solid state devices like light emitting diodes39,40 and solar cells,41,42 where the polymer works as the anode or hole injecting layer, to electrochemically active structures, such as electrochromic displays,14,27 electrochemical transistors and logics,15,16 sensors,17,43,44 bio-electrodes45,46 etc.

Figure 8. a. poly(3,4-ethylenedioxythiophene) (PEDOT). b. poly(styrenesulfonate) (PSS)
The mechanical and chemical stability of PEDOT:PSS films in combination with good electrochromic properties and high conductivity make the material an excellent base for all-organic electrochemical displays. A film of PEDOT:PSS can be reversibly switched between the oxidized and neutral state several times. PEDOT:PSS is almost transparent in the oxidized doped state and dark blue in the neutral semiconducting state, as seen from the absorbance spectrum in Figure 9. Electrochromic displays with PEDOT:PSS on paper and plastic are discussed in detail in 4.7 and Paper 3.

![Absorbance spectrum of PEDOT:PSS film in the neutral and oxidized (p-doped) state.](image)

### 2.4.3 Polyaniline

A very important group of conjugated polymers are the polyanilines. The first polyaniline (PANI), also called aniline black, was prepared in the early 19th century but the material was usually an unwanted deposit on the anode during electrolysis with aniline. In 1910, Green and Woodhead managed to control the synthesis of PANI and also started to characterize the polymer. Due to the cheap raw material, stable conducting forms, strong electrochromism and ease of processing, PANI has been a popular material in industry and science ever since.38,48
PANI is a complex conjugated polymer since the material has a number of intrinsic oxidation states and several routes of doping. Fully reduced PANI is transparent and called leucoemeraldine, with a chemical structure as shown in Figure 10a. The dark blue semi-oxidized (~50%) state is named emeraldine base (Figure 10b) and the violet blue fully oxidized material is termed pernigraniline base (Figure 10c). Contrary to most other polyaromatics, none of these states are electronically conducting, not even the fully oxidized pernigraniline form. Instead, PANI becomes conducting when the oxidized states are protonated and a green emeraldine salt is formed. This highly conducting doped form, shown in Figure 10d, can actually be reached through two completely different pathways. If the emeraldine base is treated with e.g. hydrochloric acid, protonic acid doping occurs as protonation of the imine nitrogen atoms (\(\overset{\equiv}{\text{N}}\)) creates positively charged protonated imines (\(\overset{+}{\text{NH}}\)), balanced by negative ions from the acid. This is so called non-redox doping, but in another route, chemical or electrochemical doping of the reduced leucoemeraldine base can also be utilized to obtain the very same conducting salt.\(^{18,38,48-50}\)

The nonconductive emeraldine base is soluble in N-methyl-pyrrolidone but the conducting salt, protonated with hydrochloric acid, is insoluble in organic solvents. One way to achieve a soluble (emulsion) conducting PANI salt, without incorporating covalent side chains, is to dope the material with surfactant alkyl sulfonic acids that donate protons to the polymer.\(^{51,52}\) This way of preparing the p-doped material also results in a slightly different chemical composition. Apart from the larger surfactant counter ions, which of course affect solubility and film formation, protonated amine units (\(\overset{+}{\text{NH}_2}\)) have also been detected along with the imine dittos in these systems.\(^{48,53,54}\) The effect of the surfactant counter ion on the surface properties of such a system is a key element in the wettability switch, described in 4.5, 4.6, Paper 1 and Paper 2.
Conducting Polymers

Figure 10. Polyaniline (PANI) oxidation states. a. Leucoemeraldine. b. Emeraldine base. c. Pernigraniline. d. Protonated emeraldine salt (charge balancing counter ions not shown). The dots represent unpaired electrons (radicals) coupled to the polaron lattice.

The electrochromic properties of PANI makes it a suitable candidate for multi-color electrochromic displays.24 Other areas of application include antistatic coatings and corrosion protection,55,56 biomaterials,57,58 light emitting diodes,59,60 sensors,61,62 field effect transistors63 and batteries.64
3. **Surface Energy – Wettability**

The formation and characteristics of interfaces between liquids and solids depend on the surface properties of the involved materials. Wetting behavior can therefore be valuable information in a number of scientific and industrial areas. For small volumes, surface effects are even more pronounced and surface science is therefore a crucial part of micro- and nanotechnology. Examples of application areas depending on (and utilizing) wettability are e.g.:

- **Micro-fluidics** – *How do small volumes of a liquid move on a surface or in a channel?*

- **Control of surface treatments and cleaning steps** – *Is the surface clean?*

- **Anti-fouling surfaces** – *Why are the leaves of the lotus plant always dry?*

- **Biomaterials** – *How will the biomaterial interact with human tissue?*

- **Pharmaceuticals** – *How will the drug particles dissolve and be absorbed in the body?*

- **Composites** – *What can be mixed in what?*

- **Printing technologies** – *How will the ink adhere and spread on the paper coating?*
3.1 Surface tension in theory

The molecules at the surface of a liquid or a solid behave differently from their counterparts in the bulk since they lack neighbors in one direction. The surface therefore has “free energy” in the interface towards the surrounding media and it is, neglecting other forces, energetically favorable to decrease the surface area as much as possible. This is why liquids form spherical (lowest area/volume ratio) droplets in e.g. air.

The surface energy, $\gamma$, is characteristic for a solid or liquid material in the interface towards a specified gas phase, such as air (with vapor). The surface energy determines the energy needed to increase the area of the surface, i.e. high surface energy means strong attraction between the surface molecules of a material. For liquid-gas interfaces, the surface energy is generally referred to as the surface tension (interfacial tension). A common example of surface tension and surface energy is that of a thin rectangular frame of width $l$, pulled through a liquid-gas interface, e.g. water-air, as drawn schematically in Figure 11 (from ref. 65).

\[ \text{Figure 11. Creation of a thin liquid film by pulling a wire frame through an air-water interface.} \]
A thin film of liquid may be formed in the frame and a certain force is then needed to lift the rectangle (the weight of the frame and film are not considered here). If \( \gamma \) is the force per unit length to create the new interface (interfacial tension), the force needed to move the frame (and thereby create two new interfaces, one on each side of the liquid film) can be written as:

\[
F = 2\gamma l \tag{1}
\]

If the frame is moved a short distance, \( dx/2 \), the amount of work done is given by:

\[
dW = \gamma l dx \tag{2}
\]

If the change in area, \( A \), of the liquid film is considered instead, \( \gamma \) has the units of energy per unit area (surface energy) and equation (2) can be written as:

\[
dW = \gamma dA \tag{3}
\]

This shows that \( \gamma \) can be thought of as either an interfacial tension or as a surface energy, the quantities are identical. The SI unit for surface energy / surface tension is \( \text{Nm/m}^2 = \text{N/m} \). The surface tension can be divided into polar (permanent dipoles) and dispersive (induced dipoles) parts. Polar materials, like water, typically have strong bonds between the molecules and therefore show high surface tensions in air.

### 3.2 Contact angle measurements

When a small volume of liquid is placed on a solid surface in e.g. air, the equilibrium state between the two materials and the surrounding vapor corresponds to the shape of the liquid droplet. In a simplified picture, the free energy of the solid surface can be seen as a force that will tend to spread the liquid droplet in order to decrease the solid-vapor interface. On the other hand, there is a cost in energy to form a new liquid-solid interface and therefore the interfacial energy between the liquid and solid works as a force in the opposite
Surface Energy - Wettability

direction. Finally, the surface tension of the liquid tries to contract the droplet in order to decrease the liquid-vapor interfacial area and is therefore a third force, parallel to the tangent of the droplet. The shape of the droplet can be seen as the equilibrium between these forces as shown in Figure 12. The solid surface energy in the surrounding vapor is denoted $\gamma_{sv}$, the liquid-vapor surface tension $\gamma_{lv}$ and the solid-liquid interfacial energy $\gamma_{sl}$.\textsuperscript{65,66}

![Diagram of surface tensions and contact angle](image)

**Figure 12.** Surface tensions ($\gamma$) and contact angle ($\theta$) when a liquid droplet is placed on a solid surface in the vapor atmosphere.

The angle between the solid surface and the droplet tangent is called the contact angle, $\theta$, and is a direct measure of how a liquid wets a solid (Figure 12). The relationship between the surface tensions and the contact angle is expressed in the Young-Dupré equation.\textsuperscript{65,66}

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (4)$$

Contact angle measurements are fairly simple in practice, but since the technique is very surface sensitive, cleanliness is extremely important. The most common instrument used to determine contact angles is called a goniometer. It usually consists of a sample table, a syringe for dispensing the liquid and a microscope lens or a camera to evaluate the contact angles (Figure 13). If the system has a camera connected to a computer, several images can of course be recorded over time and contact angle values are then generated from the
recorded images by software. When the liquid drop is created at the tip of the syringe, which is then lowered down until the drop contacts the solid surface, the measured contact angle is “static”. If nothing else is stated, contact angle values are generally from static measurements.

Figure 13. Photograph of goniometer. Liquid droplets for contact angle measurements are applied to the solid surface with the syringe. The camera takes pictures of the droplets and computer software can then evaluate the images.

If the volume of the liquid droplet is increased while in contact with the surface, the tangent line moves away from the syringe and the measured angle is called the “advancing” contact angle. If the volume is instead decreased in a similar fashion, the contact angle is “receding”. In many cases, there is a hysteresis between the advancing and receding contact angle values. The advancing angle is always equal to or larger than the receding and the difference could originate from e.g. contaminated surfaces or liquids, surface roughness or surface
immobility.\textsuperscript{66} One example of obvious hysteresis is a water droplet sliding down a dirty windowpane. The front of the droplet is slightly pinned to the window and therefore forms a large advancing contact angle as gravity drags the water down. Similarly, if the back of the droplet is stuck, it will form a small receding angle against the glass.

In many cases, water is used as the standard liquid when measuring contact angles. A surface that water wets (low contact angle) is called hydrophilic, while materials with high water contact angles are labelled hydrophobic. From Figure 12, one can see that a high solid surface energy will result in low contact angles and vice versa. The absolute value of the solid surface energy cannot be measured directly but is possible to estimate with contact angles from several liquids. A series of homologous liquids, such as alkanes of different length, can be used to create a so-called Zisman plot. The cosines of the contact angles are plotted against the surface tensions of the liquids to give a linear relation. The “critical surface tension” corresponding to $\cos \theta = 1$ can be extrapolated from the plot and this value gives a good estimation of the surface energy of the material studied.\textsuperscript{65,66}

Another approach is to use contact angles from two or more measurement liquids, of which one should be mainly polar and one non-polar. The intermolecular energy is the sum of the polar and dispersive component and this relationship also holds for the surface tensions. The polar and dispersive part of the solid surface energy can therefore be evaluated by e.g. the geometric mean equation ($\gamma^p$ denotes the polar and $\gamma^d$ the dispersive parts of the interfacial tensions):

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \left[ \sqrt{\left( \gamma^d_{LV} \gamma^d_{SV} \right)} + \sqrt{\left( \gamma^p_{LV} \gamma^p_{SV} \right)} \right]$$

Equation (4) and (5) give:

$$\gamma_{LV} (1 + \cos \theta) = 2 \left[ \sqrt{\left( \gamma^d_{LV} \gamma^d_{SV} \right)} + \sqrt{\left( \gamma^p_{LV} \gamma^p_{SV} \right)} \right]$$

Equation (6)
If the contact angles have been measured with at least two liquids, which have known polar and dispersive liquid-vapor interfacial tensions, equation (6) can be used to solve for the solid surface energy components.\textsuperscript{67}

A liquid on a solid surface should find it energetically favorable to move from an area with lower wettability (high contact angle) towards higher wettability (decreased contact angle).\textsuperscript{68,69} Therefore, transitions from wetting to non-wetting regions are very important in microfluidic applications in order to guide and regulate the liquid flow on the surface. Several publications on how to switch the contact angle of a surface have been presented in the last few years. The external stimuli can be e.g. temperature,\textsuperscript{70} light,\textsuperscript{71} electric fields\textsuperscript{72} or electrochemistry.\textsuperscript{73} The use of conjugated polymers to regulate wetting in all-organic devices is presented in 4.5, 4.6, Paper 1 and Paper 2.

Apart from the surface energy of the solid material, the surface topography can also affect the wetting behavior. A structured surface with high roughness will decrease the water contact angles compared to a smooth material if the original contact angle is less than 90°. The topography of the surface then forms small capillaries for the water. The liquid can penetrate the micro channels and will therefore quickly wet the surface. If the angle is larger than 90°, the uneven surface will instead result in much higher angles. In this case the water cannot enter the capillaries and has to form larger angles to the available solid surface. The effect of surface roughness on contact angle measurements can be estimated with the simple Wensel equation (7), where \( r \) denotes the surface roughness (defined as the ratio of the true area of the solid to the apparent area), \( \theta' \) the measured contact angle and \( \theta \) the “true” contact angle.\textsuperscript{65,66}

\[
r = \frac{\cos \theta'}{\cos \theta}
\]  

The creation of rough surfaces is a common technique to achieve superhydrophilic and superhydrophobic surfaces, artificially as well as in nature. Sun and co-workers\textsuperscript{75} have e.g. achieved reversible thermal switching of water contact angles between \(~0°\) and \(150°\). A famous example of a
superhydrophobic surface in nature is the leaf of the lotus plant (Figure 14). This ingenious structure barely gets wet when it rains and also is self-cleaning, since the water forms large contact angles and simply rolls off the rough waxy surface of the leaves.\textsuperscript{76,77}

![Lotus leaf and raindrop](image)

\textit{Figure 14.} Lotus leaf and raindrop. Used with permission from Victoria-adventure\textsuperscript{74} and the photographer Byoung Sup Ghill (Copyright ©)

### 3.3 Other techniques to study surface tension

#### 3.3.1 Pendant drop

The surface tension of a liquid (in e.g. air) or the interfacial tension between liquids can be calculated directly from the shape of a drop, which hangs from the syringe in the surrounding media. The shape of the drop (Figure 15) is mathematically described by three first order differential equations (8-10).\textsuperscript{78,79}
\[
\frac{dx}{ds} = \cos \phi \quad (8)
\]
\[
\frac{dz}{ds} = \sin \phi \quad (9)
\]
\[
\frac{d\phi}{ds} = 2 + \beta z - \frac{\sin \phi}{x} \quad (10)
\]
\[
\beta = \frac{\Delta \rho g R_0^3}{\gamma} \quad (11)
\]

\(x\) and \(z\) are coordinates of a point on the drop profile divided by \(R_0\), the radius of curvature at the apex, which makes them dimensionless. \(\phi\) is the turning angle at that point and \(s\) is the dimensionless curvature length from apex to the same point. The shape of the droplet is characterized by \(\beta\), which is defined in equation (11), where \(\Delta \rho\) is the difference in density between the phases and \(g\) is the gravitational constant.\(^{78,79}\)

*Figure 15. The pendant drop coordinate system.*
From a digital image of the droplet, acquired with e.g. a goniometer, computer software can quickly solve the system of differential equations numerically to best fit the droplet shape (with the same methods as when analyzing contact angles). If the liquid (and gas) densities are known, the surface tension can then be extracted. The pendant drop method has the advantage of being independent of the liquid contact angle to the solid support (as oppose to tensiometry, which is described below) and gives quick accurate values of surface tensions. Evaluating the surface tension of a liquid before using it for contact angle measurements is a good way to check for possible contamination.

### 3.3.2 Tensiometry

A classical technique to measure surface tension and interfacial interactions is tensiometry.\textsuperscript{80,81} The principle of tensiometry is the same as in the simplified example with the rectangular frame described in 3.1, i.e. the force exerted when a solid probe interacts with a surface or interface is a measure of the involved interfacial tensions. Apart from the surface tension of the analyzed liquid, the forces will depend on the size and shape of the probe as well as the contact angle between the liquid and the probe. Different shapes and types of probes can be used, but the most common are rings and plates. The results from tensiometric measurements are often very accurate and objective, but the technique requires a fair amount of the liquid to be analyzed and if the solid is studied, it has to be of a regular shape with the same surface on all areas that contact the liquid.
4. ELECTROCHEMICAL DEVICES

Since many conjugated polymers can be doped and undoped by electrochemical reactions and thereby change intrinsic properties like color, conductivity and wettability, these materials are well suited for use in different electrochemical devices. The three papers included in this thesis (and many others, e.g. ref. 14,15,17,82,83) all originate from similar simple electrochemical devices, easily manufactured on flexible substrates with “printable” materials and developed in cooperation between the group of Organic Electronics and Acreo AB. These devices will therefore be described in the sections below.

4.1 Reduction and oxidation of conducting polymers

An electrochemical reaction means that a chemical phenomena is associated with charge separation of some sort, often charge transfer. Two or more half-reactions have to take place, one oxidation and one reduction. In a simple two-electrode electrochemical cell (Figure 16), the electrodes are separated in space but linked by two conducting paths. The electrolyte between the electrodes can transport ionic charges and the conducting wires of course conduct electrons. The electrodes may either work as inert sources and sinks for electrons transferred to and from species in solution, or take part in the electrode reaction itself. If the sum of the free energy changes at both electrodes is negative (energy released), the cell works as a battery. If it is positive, a bias voltage can be applied to drive the electrochemical reaction (as in Figure 16).
Many conducting polymers can be either n-doped by reduction (addition of electrons to the polymer) or p-doped by oxidation (withdrawal of electrons from the polymer), as shown in reaction (12) and (13), respectively. P denotes the polymer, M means one or many cations (positively charged) and A stands for one or many anions (negatively charged).

\[
P^0 + xe^- + M^{++} \rightarrow P^{x-}M^{x+} \quad (12)
\]

\[
P^0 + A^{\sim} \rightarrow P^{+}A^{-} + ye^- \quad (13)
\]

However, n-doped conjugated polymers are often not as chemically stable as p-doped polymers, if oxygen or water are present, and therefore the polymer systems used in electrochemical devices are often switched between a neutral (undoped) and an oxidized (p-doped) state. As an example, commercially available PEDOT:PSS (2.4.2) is originally (pristine state) conducting and partially oxidized. From here the material can either be further oxidized to a more conducting material or reduced to the semi-conducting neutral polymer. The reactions are reversible in both directions, which makes the polymer system.
very popular for electrochemical devices. The reduction (left to right) and oxidation (right to left) of PEDOT:PSS can be written as:

\[
PEDOT^+ : PSS^- + e^- + M^+ \leftrightarrow PEDOT^0 + PSS^- M^+ \tag{14}
\]

An electrochemical technique such as voltammetry, i.e. the applied potential is swept and the current measured, is a common way to characterize conducting polymers. The oxidation potential is a measure of how much energy is needed to withdraw electrons from the polymer HOMO level and the reduction potential is at the same time a characteristic of the LUMO. The measurement is performed with a potentiostat and a three-electrode system. The reaction to be studied happens at the working electrode. A reference electrode, such as Ag/AgCl, with a well-defined electrochemical potential is used to keep the working electrode at a constant absolute potential. To maintain the potential as stable as possible, a third auxiliary electrode (counter electrode) is used to pass the current. The counter electrode is often made of Pt and should have a large active area. If reduction occurs at the working electrode the auxiliary electrode is reduced and vice versa.

The potentiostat can also be used to create polymeric materials on an electrode by electropolymerization. The monomer is then present in the electrolyte and when a potential is applied, oxidation or reduction of the monomer can create reactive radicals. Several radicals can connect to form polymeric chains and since the reaction happens at the working electrode, the polymeric film will cover that surface.

When manufacturing organic electrochemical devices, the structures should preferably be free-standing and in the best case printable. Therefore the design of the electrochemical cell is somewhat different than that shown in Figure 16. The electrolyte is generally solid or gel-like instead of a liquid solution. Conducting polymer materials work as one or several electrodes but may also function as electronic (and in some cases ionic) conductors. The polymers can e.g. be spin-coated on the substrate but are, as in the case of PEDOT:PSS, sometimes commercially available in rolls of pre-coated films on plastic or...
Electrochemical Devices

paper. The devices often have a lateral configuration, i.e. the electrodes are situated in the same plane with electrolyte on top or underneath. Patterning of the polymer films is generally done by simply cutting non-conducting lines or by over-oxidation (electrochemically destroying the conductivity of the material). For smaller structures, photolithographic techniques may also be used to manufacture the devices.

4.2 “Structure 1”

If an electrolyte is cast to cover a stripe of polymer film, made from a conducting polymer-counter ion system like PEDOT:PSS, the resulting device is referred to as “Structure 1”. If a voltage is applied along the polymer film, as shown in Figure 17, a gradient in oxidation state and color will appear.

![Figure 17. Structure 1. a. Side view with electronic and ionic conduction paths. b. Top view.](image-url)
There are two parallel paths for charge transfer in the system. The polymer film is conducting, which means that electrons can move through the material, which then works as a resistor. Since the polymer is not a perfect electronic conductor, there is always a potential difference between the two sides of the polymer stripe when a voltage is applied. Therefore, with the electrolyte on top, the positive side of the polymer will start to be oxidized and the negative side reduced. As long as the electrochemical reaction occurs in the polymer film, charges can be transported as ions through the electrolyte. Reduction of the polymer film drastically increases the impedance locally and thereby makes it more difficult for current to pass straight through the “resistor”. More reduction and oxidation will then take place as the oxidation gradient builds up. This behavior of the “Structure 1” is responsible for the saturation of drain-source current in the electrochemical transistor by Nilsson et al.\textsuperscript{15}

**4.3 “Structure 2”**

If the polymer film of Structure 1 is instead divided in two electrodes by a non-conducting line, “Structure 2” has been created, as shown in Figure 18. Electrochemically, Structure 2 is a direct equivalent to the electrochemical cell in Figure 16. The two electrodes are electronically isolated and ionic transfer is the only path for charge transport. When a bias voltage is applied, the negative electrode will start to be reduced and the positive electrode oxidized. If the voltage is subsequently removed, there is no closed circuit for the electrons to go back and the electrodes will therefore keep their respective oxidation states (until chemically affected by e.g. oxygen). With electrochromic materials such as PEDOT:PSS or PANI:DBSA (polyaniline:dodecylbenzene sulfonic acid), Structure 2 works as a very simple display pixel and several such structures can, in combination with electrochemical transistors, build up all-organic matrix-addressable displays.\textsuperscript{14} Improvement of optical contrast in PEDOT:PSS paper display pixels is discussed in \textit{4.7} and \textbf{Paper 3}. Structure 2 is also the basis for the bi-stable electrochemical wettability switch (\textit{4.5} and \textbf{Paper 1}) and works as the gate in the electrochemical transistor.\textsuperscript{15}
4.4 “Structure 3”

The device called “Structure 3” is slightly more complicated than the previously described configurations. In this case, the polymer film is divided in three pieces by non-conducting lines, as shown in Figure 19, but only the outer two segments work as electrodes. When a voltage is applied between the two electronic contacts, there are several paths for charge transport. Because of the bias voltage, the electrodes are oxidized and reduced respectively, and ions are transported between them, in the same way as seen for Structure 2 (Figure 18). Parallel to this charge transport, the middle segment of conjugated polymer is also capable of conducting electrons if ion to electron transduction can take place through oxidation on one side and reduction on the other. Therefore, an electrochemical gradient will be induced in the middle piece of Structure 3 when the electrodes are biased. The electrochemical gradient only exists as long as...
electrochemistry occurs at the electrodes. If the voltage is disconnected or the electrode material is consumed, the outer pieces of polymer will stay oxidized and reduced but the gradient in the middle will disappear.

**Figure 19.** Structure 3. **a.** Side view with electronic and ionic conduction paths. **b.** Top view.

The induced oxidation gradient is a result of the local electric field in the electrolyte and can therefore, as cleverly shown by Said and co-workers, be used to map electric fields in the electrolyte. When the conducting polymer is PANI:DBSA, the oxidation gradient is also a wettability gradient, which can be used to control the spreading of water droplets on the polymer surface (**4.5, 4.6, Paper 1** and **Paper 2**).
4.5 Electrochemical wettability switch

As mentioned in chapter 3, many physical processes are governed by surface interactions and it is therefore crucial to have control of the surface properties in numerous applications. When a conjugated polymer is oxidized or reduced, the bulk properties, such as color and conductivity, change as a result of the chemical reorganization in the material, but what happens at the surface? It turns out that the wettability or water contact angle of the polymer surface will in fact often be modified along with the oxidation state (see also Paper 1).

In undoped or neutral polymer systems, e.g. polyalkylthiophenes, doping will induce dipoles at the surface and thereby generally increase the surface tension of the material (polar materials often have high surface tension / low water contact angles). More complex systems, such as PANI doped with dodecylbenzene sulfonic acid (PANI:DBSA, Figure 20), which have a surfactant (one hydrophobic and one hydrophilic end) as the charge-balancing counter-ion, can actually work the other way around.

![Figure 20](image)

**Figure 20.** Polyaniline salt doped with dodecylbenzene sulfonic acid (PANI:DBSA). **a.** PANI:DBSA with x undoped amine groups, y protonated imines and z protonated amines. **b.** DBSA chemical structure with the hydrophilic sulfonic acid group and the hydrophobic 12-carbon alkyl chain.
When PANI is fully reduced (leucoemeraldine), the DBSA molecules are not bound to the polymer chain and can show their water-loving parts at the surface when water is placed on top. This means that the material will be hydrophilic and give low water contact angles. If, on the other hand, PANI is oxidized to a doped state (dark blue pernigraniline), the hydrophilic sulfonic acid groups of DBSA bind ionically to the polymer backbone and the hydrophobic alkyl chains are instead exposed at the surface. Therefore the oxidized polymer film shows a more hydrophobic behavior (see Figure 20 and 21).

![Figure 21. The structure 2 electrochemical wettability switch. a. PANI:DBSA wettability switch. b. Water contact angles on oxidized and reduced PANI:DBSA.](image)

The electrochemical wettability switch utilizes the control of the oxidation state of a polymer film via an applied potential. If the oxidation state of the material also determines the surface wettability, it is thereby possible to electronically...
control the latter. The simplest wettability switch is Structure 2 with PANI:DBSA as the polymer film (Figure 21a). The difference compared to the Structure 2 in Figure 18 is that, in this case, the electrolyte has been placed underneath the polymer film in order to expose the active surface to the surrounding environment. When a bias voltage is applied, one of the PANI:DBSA electrodes will switch to the yellow reduced state and the other to the dark blue oxidized state. Since both states of the polymer are moderately conducting, the switch is reversible. If water contact angles are measured on each of the surfaces, it is clear that the applied voltage has modified the surface wettability (see contact angles in Figure 21b). Since the oxidation state of the polymer system also changes the color of the material, it is possible to optically determine which contact angle the surface has. The relationship between water contact angle, absolute oxidation potential (versus a Ag/AgCl reference electrode) and optical absorbance (at 700 nm, where the difference in absorbance between oxidation states is large) for a PANI:DBSA electrochemical wettability switch is shown in Figure 22.

**Figure 22.** PANI:DBSA contact angle versus oxidation potential and absorbance at 700nm.
4.6 Electronic modulation of wettability gradients

In the same manner as the device described above, it is also possible to make a PANI:DBSA Structure 3 wettability switch. When the outer electrodes are biased, an oxidation, color and wettability (water contact angle) gradient is induced in the middle polymer section. If a drop of water is placed on the wettability gradient, it will automatically move or spread towards the reduced hydrophilic side.

If the polymer film is divided into four electrodes (4-terminal electrochemical wettability switch), it is possible to modulate the level of an induced wettability gradient with a bi-stable Structure 2 voltage. As seen in Figure 23, electrodes A and D form Structure 2, while B, D and C combine to Structure 3. D is thus common for both substructures and this is where the gradient will be formed (see also Paper 2).

![Figure 23. 4-terminal electrochemical wettability switch. Electrodes A and D form structure 2, while B, C and D constitute Structure 3. The bi-stable voltage $V_{ad}$ will modulate the oxidation state, color and wettability in D, while $V_{bc}$ controls the gradient.]

When a bias voltage, $V_{ad}$ (~3 V), is applied between A and D, the electrode chosen to be positive will be oxidized and the negative electrode will thereby be
reduced. If $V_{ad}$ is disconnected and another potential, $V_{bc}$ (~15 V), is subsequently applied between B and C (along “Structure 3”), a gradient in oxidation, color and wettability will be induced at electrode D. Since the A-D structure is bi-stable, the previously applied voltage will determine the average level of oxidation in electrode D, also when the gradient has been created. The gradient will therefore take different forms depending on $V_{ad}$, for the same $V_{bc}$. The wettability along D is thus also determined by $V_{ad}$, which means that spreading of water on the polymer surface can be modulated by the small bi-stable voltage. If D is initially oxidized (positive $V_{ad}$), water droplets placed in the center of the induced gradient will hardly move at all, but for negative $V_{ad}$, the water spreads quickly towards the reduced side.

Figure 24 shows how the color profile of the oxidation gradient in one device is modulated with three $V_{ad}$. Figure 25 compares water movement on three gradients controlled with different bi-stable potentials (three devices).

*Figure 24. Color gradient at electrode D of a 4-terminal electrochemical wettability switch, modulated with different $V_{ad}$. Approximate corresponding water contact angles are shown on the right-hand side y-axis. $V_{bc} = 15$ V*
Figure 25. Droplet movement on the surface of electrode D in a 4-terminal electrochemical wettability switch, modulated with different $V_{ad}$. $V_{bc} = 15 \text{ V}$ a. Droplet movement for three $V_{ad}$ (three devices). b. Photographs of droplet movement.
4.7 PEDOT:PSS displays with improved optical contrast

Electrochromic pixels consisting of PEDOT:PSS on plastic or paper are very promising for all-organic printed displays. Pixel elements (Structure 2, see 4.3) can be combined with electrochemical transistors to build active matrix-addressed displays or simply be individually contacted in e.g. a 7-segment device (Figure 26a). PEDOT:PSS is a suitable base-material for simple organic printable displays, since the pre-coated polymer films are environmentally stable and can be patterned in various ways (see e.g. ref. 3). It is also possible to process the polymer material from “solution” (actually emulsion), which gives additional flexibility when taking the manufacturing to a real printing press (Figure 26b).

![Figure 26. Printable displays. a. Two lateral seven segment displays on paper, patterned on the same piece of PEDOT:PSS. b. Printing press for organic electronics with printed test pattern. Both photos copyright © Niclas Kindahl, Fotofabriken and Acreo AB.](image)

PEDOT:PSS shows fast and reversible electrochromic switching but, as can be seen from Figure 9, the absorption of the colored reduced state does not cover the entire visible spectrum (400-800 nm). The lack of absorption around and below 550 nm, where our eyes are very sensitive, gives a relatively low perceived
optical contrast compared to many other electrochromic systems. One possible solution to this problem is to add another polymer film directly on top of PEDOT:PSS in Structure 2. Apart from proper processability, mechanical stability and good adhesion to the PEDOT:PSS layer, the second polymer needs the following properties in order to improve the function of the displays:

- The polymer should absorb light between 400 and 550 nm in the reduced (neutral) state and be transparent when oxidized.

- The polymer film needs good ionic conductivity for fast switching of the display. Electronic conductivity is not as crucial, since that is provided by PEDOT:PSS in the lateral direction.

- The oxidation potential has to be sufficiently low, with printable water-based electrolytes, to enable oxidation without risking over-oxidation (irreversible loss of conductivity in the material).

Several conjugated polymers, synthesized by the group of Mats Andersson at Chalmers University of Technology in Gothenburg, have been tested as candidates for the contrast-enhancing layer. The chemical structures are outlined in Figure 27 and the optical absorption upon switching each material in a two-electrode setup is shown in Figure 28.

From spectroscopic and electrochemical characterizations (details in Paper 3), two main design criteria for the second polymer layer can be suggested. First, oligo(ethylene oxide) side chains seem to increase the ionic conductivity of the polymer layer. This is expected, since oligo(ethylene oxide) prevents crystallization of the polymer molecules and therefore is commonly used in solid polymer electrolytes. Second, polymers with ethylenedioxythiophene (EDOT, as in the PEDOT monomer, Figure 8a) moieties show lower oxidation potentials and can therefore be reversibly switched in the water-based electrolyte without over-oxidation. Polymers III and IV fulfill these criteria and become transparent when oxidized, which means that they are well-suited for use in the contrast-enhancing layers.
**Figure 27.** Conjugated polymers for a contrast-enhancing layer on PEDOT:PSS displays.

**Figure 28.** Optical absorbance of polymers in Figure 27 at different applied potentials in a two-electrode setup.
Organic flexible displays with polymer III and IV, respectively, on PEDOT:PSS have been created and characterized with spectrophotometry. As shown in Figure 29, the optical contrast, defined as the change in luminance $\Delta L^*$ (details in Paper 3), is almost doubled by the addition of a second polymer layer.

**Figure 29.** Optical absorbance of flexible organic PEDOT:PSS displays with and without contrast-enhancement layer. $\Delta L^*$ denotes the optical contrast. **a.** Only PEDOT:PSS. **b.** PEDOT:PSS plus polymer III. **c.** PEDOT:PSS plus polymer IV.
5. ONGOING AND FUTURE WORK

5.1 BioX

Due to their organic chemical composition and relatively soft mechanical properties, conjugated polymers generally work well as biocompatible materials. This, in combination with the fact that the polymers use both electrons and ions as charge carriers, make this class of materials very interesting for studying and possibly manipulating cell signaling. Our living cells often use only a few common ions, such as potassium and calcium, when communication internally and with each other. The internal ionic concentrations in some cases oscillate at specific frequencies as a response to external stimuli and thereby induce several activities, e.g. gene expression, in the cell.\textsuperscript{90} If the ion transport to and from the cell could be controlled electronically it would be possible not only to study in detail how cells interact with each other and the surrounding environment but also to stimulate different responses.

One task for the future is to trigger cellular responses with the use of organic electronics and ongoing work focuses on communication with cells that grow on films of PEDOT:PSS. The work is performed by the Organic Electronics group in cooperation with the group of Agneta Richter-Dahlfors at Karolinska Institutet. Preliminary results show that the studied cell-type can adhere and live on PEDOT:PSS and signs of electronic stimulation have also been detected.
5.2 Wettability switch

The work with electronic wettability switching will also continue. Ongoing and future tasks include switching with different materials and surface topographies, preferably with high water contact angles to enable movement of droplets rather than spreading of liquids on the surface. Another focus is to utilize the wettability switches with simple microfluidic channels in order to make electronically controlled liquid gates.

Preliminary results show that by choosing the right polymer system with appropriate side groups, it is possible to tune the oxidized and reduced contact angles to achieve wettability switching in the desired region of hydrophilicity. Initial work with microfluidic channels on polyalkythiophene wettability switches, performed by Linda Robinson and Anders Hentzell, also indicates that the change in contact angle is, with the right experimental conditions, enough to control water flow in the channels.
REFERENCES


References


References


84. [http://www.orgel.itn.liu.se/](http://www.orgel.itn.liu.se/).


