Charge Transport Modulation and Optical Absorption Switching in Organic Electronic Devices

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Norrköping 2007
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This work was funded by the Royal Swedish Academy of Sciences (KVA), the Swedish Foundation for Strategic Research (SSF) and the Swedish Research Council (VR).

Linköping Studies in Science and Technology. Dissertations, No. 1147
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ISSN: 0345-7524
Printed by LiU-Tryck, Linköping, Sweden, 2007
Cover: illustration summarizing the contributions to the thesis
“Tired of staring at the same four walls? Cream is so 1990s. Would a lick of
paint help? Don't reach for the brush just yet. With electronic wallpaper, your
chameleonic walls would change to suit the mood or occasion.”

Quotation from Jonathan Fildes’ introduction in the “Electric Paper” article,
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Abstract

Organic electronics has evolved into a well-established research field thanks to major progresses in material sciences during recent decades. More attention was paid to this research field when “the discovery and development of conductive polymers” was awarded the Nobel Prize in Chemistry in 2000. Electronic devices that rely on tailor-made material functionalities, the ability of solution processing and low-cost manufacturing on flexible substrates by traditional printing techniques are among the key features in organic electronics. The common theme while exploring organic electronics, and the focus of this thesis, is that (semi-)conducting polymers serve as active materials to define the principle of operation in devices.

This thesis reviews two kinds of organic electronic devices. The first part describes electrochemical devices based on conducting polymers. Active matrix addressed displays that are printed on flexible substrates have been obtained by arranging electrochemical smart pixels, based on the combination of electrochemical transistors and electrochromic display cells, into cross-point matrices. The resulting polymer-based active-matrix displays are operated at low voltages and the same active material is used in the electrochemical transistors as well as in the electrochromic display cells, simply by employing the opto-electronic properties of the material. In addition to this first part, a switchable optical polarizer based on electrochromism in a stretch-aligned conducting polymer is described. The second part reports switchable charge traps in polymer diodes. Here, a device based on a solid-state blend of a conjugated polymer and a photochromic molecule has been demonstrated. The solid state blend, sandwiched between two electrodes, provide a polymer diode that allows reversible current modulation between two different charge transport mechanisms via externally triggered switching of the charge trap density.
Sammanfattning


Avhandlingen berör två olika typer av elektroniska komponenter baserade på organiska material. Den ena delen handlar om elektrokemiska komponenter uppbygda av ledande polymerer. Ett användningsområde för detta är matrisadresserade displayen tryckta på vanligt papper. De aktiva komponenterna i displayen är elektrokemiska transistorer och elektrokroma displayceller, som i det här fallet härstammar från ett och samma material; en unik ledande polymer vars optiska och elektroniska egenskaper båda kan kontrolleras. Den andra delen av avhandlingen behandlar laddningstransport genom en polymerdiod där en extra funktionalitet i form av en fotokrom molekylärschakta har lagts till. Fotokromerna kan styras mellan två olika tillstånd med hjälp av våglängden på det ljus som används vid exponering, vilket i sin tur styr hur laddningarna genom dioden transporterar. Komponenten kan därför användas i sensorapplikationer där ljus av en viss våglängd ska detekteras.
Acknowledgements

Even though only one name is printed on the front of this thesis, I would not have come this far without a lot of help and support during my years as a graduate student in the Organic Electronics group. Therefore, I would like to express my sincere gratitude to:

Magnus, for all your encouraging support and optimism on new ideas, your Friday experiment spirit, your unique ability to twist disheartening results into exciting continuations and, of course, for giving me the opportunity to work in your group.

Nate, for always spending time on answering questions and for the courses you have taught.

Xavier, for the pedagogical skills that you endow to your lectures, and for providing answers and help on short time notice.

Thomas, for all valuable discussions during your time in our group and at Acreo.

Robert, for the encouragement you are devoting this technology, and for our fruitful collaboration on matrix displays.

Sophie, for always helping out with administrative duties.

David, for your long (and now restarted) mentorship related to EC devices.

Payman, for all (scientific) discussions we have had, and for always helping out in the lab.

Fredrik, for our endless discussions on new (wild and crazy) device experiments.

The Organic Electronics group, for the friendly atmosphere (around the lunch table).

The Acreo Nkpg staff, for all valuable discussions, for maintaining lab and equipment in a good shape and, of course, for kindly providing me some office space.

…and of course:

Josefine, for all your love, support and understanding during my, occasionally, late working hours. Things will, eventually, settle a bit with only one job to go to.

Elsa, my lovely daughter, for all love and happiness that you are giving me.
Papers included in the thesis

Paper 1

Active Matrix Displays Based on All-Organic Electrochemical Smart Pixels
Printed on Paper
Peter Andersson, David Nilsson, Per-Olof Svensson, Miaoxiang Chen, Anna Malmström, Tommi Remonen, Thomas Kugler and Magnus Berggren
Author’s contribution: Half of the experimental work. Wrote parts of the first draft of the manuscript and was involved in the final editing until manuscript submission.

Paper 2

Organic Electrochemical Smart Pixels
Peter Andersson, David Nilsson, Per-Olof Svensson, Miaoxiang Chen, Anna Malmström, Tommi Remonen, Thomas Kugler and Magnus Berggren
Author’s contribution: All experimental work, all manuscript writing.

Paper 3

Switchable Optical Polarizer Based on Electrochromism in Stretch-Aligned Polyaniline
Peter Andersson, Thomas Kugler and Magnus Berggren
Author’s contribution: All experimental work. Wrote the first draft of the manuscript and was involved in an iterative editing process until manuscript submission.

Paper 4

Printable All-Organic Electrochromic Active-Matrix Displays
Peter Andersson, Robert Forchheimer, Payman Tehrani and Magnus Berggren
Author’s contribution: Most of the experimental work (except for circuit simulations), most of the manuscript writing.
Paper 5

**Switchable Charge Traps in Polymer Diodes**
*Peter Andersson, Nathaniel D. Robinson and Magnus Berggren*
Advanced Materials, volume 17, number 14, pp. 1798-1803 (2005)
Author’s contribution: All experimental work. Wrote the first draft of the manuscript and was responsible for an iterative editing process until manuscript submission.

Paper 6

**Diodes Based on Blends of Molecular Switches and Conjugated Polymers**
*Peter Andersson, Nathaniel D. Robinson and Magnus Berggren*
Author’s contribution: All experimental work, all manuscript writing.
Related work not included in the thesis

The Origin of the High Conductivity of Poly(3,4-ethylenedioxythiophene)-Poly(styrenesulfonate) (PEDOT-PSS) Plastic Electrodes

Photochromic Diodes
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Electric Paper
Jonathan Fildes

Paper View TV
Ed Gerstner

Electrochemical Pixel Device
United States Patent 6642069
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1 Introduction to organic electronics

The steadily increasing desire for faster, smaller and cheaper electronic products in our society has not only encouraged the traditional inorganic semiconductor manufacturing facilities to invent and put novel electronic devices into the market, but also forced them to allocate time and financial resources on research and development to meet both customer demand and to respond to competition in between industries; the continuous strive to achieve a more efficient manufacturing process. The performance of advanced microprocessors and memories is still improving according to the famous exponential law predicted by Gordon Moore, that is, that the number of transistors placed on a chip would double in either every year (1965) or every two years (1975) [1]. However, as the feature size has become smaller than the wavelength of visible light, typically 65 nanometers in frontier technologies, limitations regarding (optical) lithography patterning and larger leakage currents in the transistors are looming. The International Technology Roadmap for Semiconductors [2] has predicted that the information technology miniaturization will continue for another few years (2010) before the optical lithography patterning method utilized today needs to be replaced.

This, together with progress in materials science research during recent decades and the desire to achieve novel functionalities in low-cost electronic devices manufactured by printing techniques, has brought the organic electronics research field to light. Examples of applications for organic materials range from high-end memory devices to low-end printable displays. The common thread in these devices is that materials such as carbon nanotubes, switchable organic molecules and conducting polymers serve as the active materials, where the two latter are in focus in this thesis.

Polymers have traditionally been used in electrical applications as the insulating material that surround metal wires in order to prevent short-circuits between conductors, primarily because most polymers are electrically insulating. However, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa changed this point of view three decades ago when they observed a tremendous conductivity increase, by a factor more than one billion, upon chemical oxidation of a polymer known as polyacetylene [3]. Since then, polymer-based organic electronics has evolved to become a well-established research field and further attention was attracted to the field in the year 2000 when the three scientists were awarded the Nobel Prize in Chemistry “for the discovery and development of conductive polymers” [4].
There is a seemingly endless number of polymeric materials available today, either synthesized by mankind or produced by nature. Despite a broad spectrum of chemical formulas and material properties possessed by various polymers, they are all built-up from monomeric units coupled to each other to form long macromolecular chains upon polymerization. The result is an amorphous material that often can be processed from solution into thin and flexible films by using spin-coating or printing production techniques. The ability to process the polymers from solution is a key factor in manufacturing flexible electronic devices at low cost. Another important feature of polymers is that their optical and electronic properties can be tailor-made via chemical synthesis and material design, which allows for novel materials containing exclusive and novel functionalities.

Various organic electronic device concepts have been developed including conjugated polymers as the active material. Examples previously reported in literature are light emitting diodes [5], light-emitting electrochemical cells [6], solar cells [7], field-effect transistors [8], lasers [9] and transistor circuits manufactured with printing techniques [10].

Furthermore, most of the electrically conducting polymers respond to electrochemical switching, a process which can be used to translate signals in between electronic and ionic entities [11]. Optical, electrical, volumetric and surface energy properties of the polymers is controlled by their electrochemical state, that is, oxidation or reduction, and these effects can be used in various electrochemical devices to define device operation. A change in optical absorption due to electrochemistry, also denoted as electrochromism, has been reported in smart windows [12, 13] and display cells [14]. A change in electrical conductivity can be achieved from the doping or de-doping process upon oxidation or reduction and this effect can be used to modulate the current through electrochemical diodes [15] and electrochemical transistors [16-18]. A volumetric change occurs when the mobile ions enter or escape the polymer, upon electrochemical switching, an effect which can be used in electroactuators for different kinds of micro-robotic systems [19]. The surface energy change is caused either by ion motion or polarization in the film and is dependent on the oxidation state of the polymer, an effect that can be used in micro-fluidics to control the motion of liquids [20]. Furthermore, an ion pump that relies on electrochemical switching of a conjugated polymer was recently demonstrated in an organic bioelectronic application. Here, specific cations (Ca$^{2+}$ and K$^+$) were transported from an electrolyte reservoir, through the polymer, and received by a target electrolyte [21].
Additionally, in parallel to the polymer electronics revolution, major research efforts have been devoted to designing and synthesizing organic molecular switches that can be transformed in between two different states upon activation by external stimuli such as temperature, electronic signals or electromagnetic radiation. The latter is used to trigger the switching mechanism of photochromic molecules, which are one kind of molecular switch materials that can be utilized in novel opto-electronic devices [22-25], actuators [26, 27], wettability switching [28] and microfluidic devices [29].

Switching in organic-based materials, to define the principle of operation in devices, is the main focus of this thesis, and the first part is about electronic and optical changes based on electrochemical switching in conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI), and how they can be utilized in novel organic electronic devices. An electrochemical smart pixel can be achieved through the combination of an electrochemical transistor and an electrochromic display cell, which use the change in electrical conductivity and optical absorption in PEDOT, respectively. Integrating such smart pixels at each intersection in cross-point matrices opens up the possibility to realize actively addressed matrix displays, manufactured by printing techniques, on flexible substrates. Furthermore, in a project that slightly deviates from active matrix addressed displays, a switchable optical polarizer based on electrochromism in stretch-aligned PANI will be briefly discussed. Orthogonal switching of the polarized optical absorption can be achieved in this device; an effect that originates from the voltage polarity that is applied to the electrochromic films in the device. The second part of the thesis is about charge transport modulation in an organic diode. This can be achieved by switching photochromic molecules that are immersed inside a semiconducting polymer host. The blend, sandwiched between two electrodes, results in a polymer diode that allows reversible modulation between two charge transport mechanisms via externally (photo-)triggered switching of the charge trap density. Hence, photons are used for information storage in this opto-electronic device, while the readout is purely electronic.
2 Conjugated polymers and photochromic molecules

2.1 Electronic structure in conjugated molecules

As previously mentioned, Heeger, MacDiarmid and Shirakawa were awarded the Nobel Prize in chemistry a few years ago for the discovery of conducting polymers [4]. Their prime observation was that by exposing oxidative iodine vapor to polyacetylene resulted in more than a billion-folded increase of its electrical conductivity [3]. The terms oxidation and reduction refer to p-doping and n-doping of the polymer, respectively, and the change in conductivity is analogous to the impact of doping in silicon or other inorganic semiconductors.

Nearly all polymers contain a backbone chain of carbon atoms. The electrical conductivity of a polymeric material, ranging from insulating, via semiconducting, to conducting depends on the electronic states formed along the polymer chain from the electrons of the carbon atoms and how these interact with each other. In addition, the charge conductivity depends on morphology, the overall chemical nature of the polymer and the attached substituents coupled to the polymer backbone. In order to provide understanding of the electronic structure and the bonding configuration in conjugated polymers, a brief description of the electronic structure of an isolated carbon atom and a dihydrogen molecule is given below.

The Pauli exclusion principle implies that two electrons in the same spatial orbital must have different spin. In an isolated atom, this implies that the electrons are separated into different atomic orbitals defining regions in space with high probability of finding an electron [30]. There are six electrons in a carbon atom; two are tightly bound to the nucleus in the 1s orbital, while the other four are valence electrons in the 2s and 2p orbitals, see Figure 1a. It is the valence electrons in carbon atoms that allow the formation of bonds and the creation of a molecule since their electron densities are farther away from the nucleus than the core (1s) electrons.

The notion of covalent bonding can be simply illustrated with the dihydrogen molecule, where each hydrogen atom carries one electron in a 1s atomic orbital. These two electrons sense the positive charges of the nuclei as the two hydrogen atoms are in close proximity to each other and two wave functions, denoted bonding and antibonding molecular orbitals, are
used to describe the presence of these electrons around the nuclei. The molecule is in its most stable state if the two electrons are represented with the binding molecular orbital, in which the two electrons have opposite spin. The occupation of a molecular bonding orbital defines a covalent bond, while the occupation of an antibonding orbital would destabilize the molecule, see Figure 1b.

![Diagram showing electronic configuration and bonding in dihydrogen molecule](image)

Figure 1. a) A schematic that shows the electronic configuration of the carbon atom ground state. b) The formation of a covalent bond in the dihydrogen molecule.

### 2.1.1 Hybridization

When two carbon atoms are brought together to form a molecule, they form hybrid orbitals due to the new potential created by the surrounding atoms. Such molecular hybrid orbitals can be described from a linear combination of the atomic orbitals. One s-orbital and three p-orbitals of the tetravalent carbon atom can be combined to form a new set of four sp³-hybridized orbitals. Following the same principle as described previously for the dihydrogen molecule, the singly occupied hybrid orbitals of carbon allow the formation of methane, CH₄, with four equivalent and symmetric bonds to hydrogen atoms. This corresponds to four bonds that are oriented in a tetrahedral structure with an angle separation of 109.5° with respect to each other. Furthermore, both sp²- and sp-hybridized orbitals can be formed. For carbon atoms in a conjugated molecule, a mixture of one s-orbital and two p-orbitals can be combined to form three sp²-hybrid orbitals. This new set of hybrid orbitals hold three bonds that are triagonally arranged in the same plane as the nucleus with a separation angle of 120°. The last possible hybridization state is obtained by the combination of one s-orbital and one p-orbital, which results in two sp-hybridized orbitals that are represented by two bonds oriented to opposite one another.
2.1.2 σ-Bonds

The hydrocarbon molecule ethane, C₂H₆, consists of two sp³-hybridized carbon atoms and six hydrogen atoms, where the latter consist of only 1s-orbitals since they have only one valence electron. The bond between a carbon atom and a hydrogen atom is formed by an overlap between one sp³-orbital of carbon and the 1s-orbital of hydrogen and the bond between the two carbon atoms arises from an overlap of two sp³-orbitals. The overlaps in the ethane molecule create seven sigma (σ) bonds. Repeating ethane molecular units results in a polymer chain known as polyethylene (C₂H₄)n; a flexible material widely used in, for example, plastic bags. Since all valence electrons are occupied and localized in σ-bonds in polyethylene, this polymer shows a purely insulating electronic property.

2.1.3 π-Bonds

The hydrocarbon molecule ethene (or ethylene), C₂H₄, consists of four hydrogen atoms and two sp²-hybridized carbon atoms that share two valence electron pairs in a double bond, which results in a total of six σ-bonds. Two valence electrons are, therefore, not yet involved in the molecular formation, that is, one valence electron per carbon atom remains in the 2p-orbital. Instead of taking part in σ-bond formation, the remaining 2p-orbitals overlap above and below the nodal plane of the σ-double bond, orthogonal to the σ-bond bond axis, as they form another type of covalent molecular interaction denoted as a pi (π) bond. Repeating several ethene molecular units results in the semiconducting polyacetylene (C₂H₂)n. Electrons that are involved in π-bonds are the key-players in semiconducting polymers since they are delocalized and have higher energies than localized σ-bond electrons. As a consequence, they can form occupied π-band and unoccupied π*-band, often referred to as the valence band and conduction band, respectively. The presence of delocalized electronic states allows a charge carrier to travel efficiently along the polymer chains under the presence of an electric field, and the resulting narrower optical band gap provides optical absorption in the visible wavelength region.

In summary, the localized electrons in the σ-bonds form the backbone in a polymer chain and dominate the mechanical properties, while the electrons in the π-bonds are delocalized along the chain and responsible for the electrical and optical properties of a conjugated polymer material. The σ-bonds form completely filled low-lying energy bands.
that have a larger energy gap (the energy between bonding and antibonding states) than the $\pi$-electrons, see Figure 2.

Figure 2. Relative energies of molecular orbitals are shown [30]. The star (*) denotes an unoccupied (antibonding) molecular orbital. $\sigma$-electrons act like a glue that holds the atoms together in the molecule, while $\pi$-electrons, that are easier to excite, provide the optical and electronic properties of the molecule.
2.2 Conjugated polymers

Saturated polymers have only single $\sigma$-bonds, and no charge transport will occur since all valence electrons are involved in $\sigma$-bonds. In contrast, conjugated polymers are unsaturated polymers with an alternation between single and double bonds that is essential for charge carrier transport. This results in the conjugated polymer chain shown in Figure 3, in which the non-hybridized valence electron in each carbon atom forms the delocalized $\pi$-bond from a neighboring overlap that is orthogonally oriented to the plane of the $\sigma$-bonding $sp^2$-orbitals.

![Figure 3. The conjugation in polyacetylene is shown as an alternation of single and double bonds along the polymer backbone.](image)

2.2.1 Optical band gap

The band gap energy in an undoped organic semiconductor is typically between 2 and 4 eV and the Fermi energy level in an intrinsic semiconductor is positioned in the middle of the band gap. Semiconducting materials have a similar structure as compared to insulators at very low temperatures, the highest occupied molecular orbital (HOMO) energy level (in the molecular picture), i.e. the top of the filled valence band (in the solid-state picture), is distinctly separated from the lowest unoccupied molecular orbital (LUMO) energy level, i.e. the low-energy states of the conduction band, by a band gap with no allowed energy state, see Figure 4. Electrons can be thermally excited to the LUMO energy level when the temperature is increased, even though this is considered negligible in most organic semiconductors due to their relatively high band gaps compared to inorganic semiconductors.
The difference in band gap energies in semiconductors and insulators, as well as the absence of a forbidden energy gap in conductors, are shown. The Fermi energy levels are positioned in the middle of the respective band gaps under the assumptions of low temperature and neutral materials without dopant species.

The exact band gap in a polymer film is not easily determined. A polymer film consists of many chains, and the energy gap can vary between these individual chains due to defects and dispersion in polymer chain lengths. Thus, the determination of the macroscopic band gap value for a polymer film is an average value derived from the energy gaps of many polymer chains. The conductivity in a polymer increases if the temperature is elevated, which is mainly due to enhanced hopping probability between available localized sites along the polymer chains and in between different chains. This is contrary to the behavior observed in metals, in which the higher degree of phonons at higher temperatures reduces the electrical conductivity by scattering of delocalized charge carriers.

### 2.2.2 Charge carriers through polymer doping

Conjugated polymers are true semiconductors in their pristine form, a character that is utilized in electronic and opto-electronic devices. In their doped form, they can reach conductivity values that are approaching those of metals. Based on this, these systems are therefore often denoted as one-dimensional synthetic metals due to the polymer chain structure. Figure 5 shows the conductivity values in various materials.
From the neutral state, conjugated polymers can be either p-doped or n-doped through an oxidation or reduction process, respectively. P-doping is much more common in polymers because n-doped polymers are less stable in air: a spontaneous transition towards the neutral state occurs via oxidation involving dioxygen. In oxidative doping, an electron is removed from the HOMO energy level of the polymer chain, that thereby becomes positively charged (stabilized locally by an anion), and such charges are then able to create electrical current by migration in the polymer film. The opposite process occurs in reductive doping; an electron is added to the LUMO energy level of the polymer chain instead of being removed from the HOMO energy level.

### 2.2.3 Solitons

Polyacetylene has two isomers: trans- or cis-isomerism, as shown in Figure 6. Trans-polyacetylene is called a degenerate system because the energy of the polymer chain is independent on the bond alternation. In contrast, a change in bond length alternation is accompanied by a destabilization of the cis-polyacetylene chain, which is denoted as a non-degenerate ground state polymer. Trans-polyacetylene is more stable than cis-polyacetylene, even though neither isomeric state is stable enough in ambient environment to be interesting from an application point of view.
Figure 6. (I) and (II) are the two degenerate forms of the trans-polyacetylene isomers. (III) and (IV) are the high and low energy states of the non-degenerate cis-polyacetylene, respectively.

In trans-polyacetylene, i.e. for a degenerate ground state polymer, neutral defects, denoted solitons, can exist if the polymer chain contains an odd number of carbon atoms. A soliton is a localized entity that separates two regions characterized with different bond length alternation, and this defect is delocalized over a few neighboring monomers, as shown in Figure 7a. The electron associated with the soliton has its energy level in the middle of the gap of the trans-polyacetylene polymer chain. Since the energy of the polymer chain remains the same upon changing the bond length alternation in degenerate ground state polymers, the soliton appears as a mobile carrier. Doping of this polymer chain forces the neutral soliton into a charged but spin-less state, where either oxidative or reductive doping corresponds to a positively or negatively charged soliton, respectively, see Figure 7b.
2.2.4 Polarons

Inorganic semiconductors can be grown to form crystalline structures. Withdrawing an electron from such a structure results in a positively charged species delocalized among many atoms within the crystal. The missing electron is, therefore, hardly noticed due to the strong delocalization effect. However, this will not be the case in polymeric materials since they are confined in a quasi-one-dimensional electronic system with an amorphous structure. Withdrawal of an electron from a polymer, i.e. injection of a hole to the polymer, breaks the \( \pi \)-bond at the location where the electron was removed. The addition of charge is accompanied by a structure modification (modification of the bond length alternation) delocalized over a few monomer units, and such charge defect is called a polaron.

Polarons are the charge carriers in conjugated polymers. Polarons are transported along one polymer chain and can, via hopping, jump between two chains, i.e. intra- and inter-chain transport can co-exist, respectively. Oxidative doping of the non-degenerate conjugated system poly(\textit{para}-phenylene vinylene) (PPV) is shown in Figure 8a. The lowest energy of this macromolecular chain is found in the aromatic ground state. Withdrawal of one electron from this neutral state creates a positively charged polaron, i.e. a radical cation, and further oxidation may form a doubly charged bi-polaron characterized by a quinoid structure. Polarons can exist in four different states, that is, positively charged polaron/bi-polaron and negatively charged polaron/bi-polaron, as shown in Figure 8b.
2.2.5 Examples of conjugated polymers

Specific electronic and optical properties of conjugated polymers can be obtained by an appropriate choice of the monomers. Polymer synthesis is often scalable to manufacture higher volumes suitable low-cost manufacturing of electronic materials. Several conjugated polymer families, all showing different characters, are available. Just a few examples are mentioned below: Polypyrrole – A conjugated polymer that undergoes a volumetric change upon electrochemical switching upon an appropriate choice of counter-ions. Based on this property, it is used as an artificial muscle in biotechnology and micro-robotic systems [19].

Figure 8. a) Oxidation of the aromatic ground state of a PPV-chain forms a charged polaron. Further oxidation results in the formation of a doubly charged bi-polaron in the excited quinoid state. Polarons and bi-polarons are responsible for the charge transport in conjugated polymer systems. b) Positive polarons and bi-polarons are obtained from oxidative doping, while the negative counterparts are resulting from a reductive doping process in which the conjugated polymer chain gains electrons.

Figure 9. The chemical structure of polypyrrole.
Polythiophene – A conjugated polymer family that primarily has been utilized in organic field effect transistors [8]. Their high charge carrier mobility is due to their planarity and tendency of aggregating to form crystalline domains.

![Polythiophene](image)

Figure 10. The chemical structure of polythiophene.

Poly(\textit{para}-phenylene vinylene) – Another conjugated polymer system that is commonly used in electroluminescent devices due to its molecular disorder that prevents luminescence quenching [5].

![Poly(\textit{para}-phenylene vinylene)](image)

Figure 11. The chemical structure of poly(\textit{para}-phenylene vinylene).
Polyaniline – A (semi)-conducting polymer that exhibits electrochemical activity and has proven to be a very successful candidate in electrochromic and other electrochemical devices. This polymer was utilized to obtain the switchable optical polarizer presented in Paper 3.

Figure 12. The chemical structures of the three different oxidation states in semiconducting polyaniline are shown. When the oxidation state, denoted $y$ in the figure, equals 1, 0.5 or 0, the polymer is in its fully reduced leucoemeraldine state, intermediate emeraldine base state or the fully oxidized pernigraniline state, respectively. Polyaniline is a unique polymer since the highly conducting emeraldine salt (not shown here) can be reached via two different doping mechanisms; chemical doping and protonation in acidic environment [32].

Poly(3,4-ethylenedioxythiophene) blended with the counter ion poly(styrene sulfonate), abbreviated PEDOT:PSS [33, 34] – This polythiophene derivative is one of the most commonly used material today in the field of organic electronics and has a key-role in this thesis since it is the active material in electrochemical transistors, the electrochromic display cells and also serves as the conducting lines in the active matrix addressed displays and the electrochemical smart pixels presented in Paper 1, Paper 2 and Paper 4.

Figure 13. The chemical structure of poly(3,4-ethylenedioxythiophene) (PEDOT) is shown to the left. The common counter ion poly(styrene sulfonate) (PSS), that is shown to the right, maintains charge neutrality when a positive charge is formed upon oxidation of PEDOT.

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2.3 Photochromic molecules

Various kinds of organic molecular switches have been designed and synthesized during recent decades with the aim of being utilized in memory applications [35, 36]. Molecular switches are triggered by an external stimulus, such as temperature, electrical signals or electromagnetic radiation. When light act as specific stimulus, the molecular switches are called photochromic molecules. The absorption of photons generates a reversible transformation, photoisomerization, between two different states that exhibit different optical absorption. The associated absorption spectra of a photochromic molecule show one high energy gap state (here denoted A) that typically absorbs in the ultraviolet region, while the low energy gap state (here denoted B) typically absorbs visible light, even though absorption in the near infrared region has been reported for photochromic molecules [37]. Light irradiation by a wavelength that coincides with the absorption spectrum of state A \( (\lambda_A^{\text{max}}) \) causes a transformation to a state B, while exposure to a wavelength that matches the B state absorption spectrum \( (\lambda_B^{\text{max}}) \) enables the reverse switching event, see Figure 14.

![Figure 14. Schematic showing the transformations between the two states of a photochromic molecule. The kT term indicates that most photochromic molecules also can be transformed back to the most stable isomer by thermal activation.](image)

While exposed to light of a specific wavelength, the photochromic molecule undergoes a geometric rearrangement that results in a change in conjugation length and an energy shift of the HOMO and/or the LUMO levels. Hence, control of electronic structure and optical energy gap (color) of the photochromic molecule can be achieved by taking advantage of this molecular drawbridge. Therefore, photochromic molecules have been used as the active switch material in opto-electronic applications such as optical storage [22, 23], electrical switch devices [24, 25] and molecular wire switches [38, 39]. Photochromic switching is not exclusively found in organic materials [40], but a few common examples of organic photochromic molecules that have been utilized in opto-electronic switch devices are the derivatives of diarylethene [41], spiropyran [42] and spirooxazine [42], where the latter has been used in Paper 5 and Paper 6. The chemical structures of these compounds are presented in Figure 15.

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Figure 15. The chemical structures of a) diarylethene, b) spiropyran and c) spirooxazine are shown. It should be noted that the open form corresponds to the transparent high energy gap state in diarylethene, while the open form instead corresponds to the colored low energy gap state in the spiro-compounds.

Photochromic molecules have successfully been explored in various kinds of optical lenses, for example in sun glasses due to their change in color upon switching in between the A and B states, but they are yet not commercially available in opto-electronic applications. This is mainly due to that the photochromic compounds should fulfill the following requirements in such devices:

- Thermal stability of both isomers
- Low fatigue
- Fast response
- Non-destructive readout
The B state of a photochromic molecule is typically thermally unstable and this results in spontaneous switching from this excited state to the ground state. Low fatigue is of equal importance since this involves chemical degradation, for example through destructive side reactions, and hence determines the life time of a photochromic molecule in a device application. Research efforts aiming for synthesis of thermally irreversible but optically reversible photochromic compounds are of crucial importance in order to achieve long retention- and life time in opto-electronic devices that operate at room temperature [42].
3 Electrochemical devices

Doped poly(3,4-ethylenedioxythiophene) (PEDOT) balanced by the counter anion poly(styrene sulfonate) (PSS), is one of the most commonly used conducting polymers due to its great stability and easy processing from water [33, 34]. Bayer and Agfa-Gevaert are mass-producing this conducting polymer primarily for antistatic coatings and as the electrodes in capacitor applications. PEDOT:PSS shows stability in ambient atmosphere, is transparent, has a high conductivity (up to 120 S/cm) and has a high work function (4.8-4.9 eV). Additionally, PEDOT-PSS can be formulated as water based inks suitable for printing manufacturing. This makes it suitable as printable electrodes for organic electronic devices [43, 44] and as the hole-injecting electrodes in solid-state organic light emitting devices [45].

Furthermore, electrochemical switching of PEDOT:PSS includes a two-folded effect where both the electrical conductivity and the optical absorption characteristics is controlled by the oxidation state of the material. Electrochemical transistors [18] and electrochemical logic circuits [46] have been presented in the past, while the combination of electrochemical transistors and electrochromic display cells arranged as smart pixels into active matrix addressed displays printed on ordinary cellulose-based paper is one of the contributions in this thesis. The latter has the attracted attention of popular science [47, 48] and is further discussed in Paper 1, Paper 2 and Paper 4. These polymer-based devices controlled by electrochemical switching are operated at low voltages and do not require critical dimensions to be patterned, unlike field-effect driven devices. Another advantage is that the very same active material (PEDOT:PSS) is used in the whole circuit, that is, in electrochemical transistors, electrochromic display cells and conducting lines, which promises easy manufacturing of all-organic and flexible active matrix addressed displays by printing techniques.

PEDOT is, in its pristine form, a semiconducting conjugated polymer with a rather low band gap below around 2 eV. The doped form of PEDOT absorbs mostly in the near infrared region, due to absorption provided by the polaron and bipolaron states (and bands) inside the band gap. The degree of doping that is required to make conjugated polymers conductive is typically very high, often reaching several tens on the percentage scale, compared with inorganic semiconductors that normally utilize doping fractions on the order of a few parts per million.
Oxidation of a PEDOT polymer chain is shown in Figure 16. Here, two electrons are withdrawn from the initially neutral PEDOT chain and a bi-polaron that carries a positive double charge is created. A large number of these charge carriers will form bi-polaronic bands within the band gap that allow for new optical transitions as well as an increased number of hopping sites improving charge transport [49]. In the oxidized state of PEDOT, the immobile anion PSS\(^-\) balances the charge and functions as the counter-ion. In the neutral state of PEDOT, PSS\(^-\) binds to a mobile cation, typically provided from an external electrolyte.

Figure 16. The upper part of the figure is the PSS chain and the lower part is the PEDOT polymer chain in the form of a bi-polaron that is carrying a positive double charge. Negatively charged ions ensure the overall charge neutrality of the doped system and bi-polarons are responsible for the charge transport.
3.1 Electrochromism in PEDOT:PSS

PEDOT:PSS belongs to the class of materials dubbed electrochromic because it changes color when oxidized or reduced. This opto-electronic property can be used to create display cells that are switchable between two different color states. The PEDOT:PSS that is utilized in most of the electrochemical devices reported here was provided by Agfa-Gevaert in Belgium under the trademark Orgacon EL-350 [50], which is a 200 nm thick semi-oxidized layer of conducting PEDOT:PSS film coated on ~ 400 m long rolls of polyester substrate. PEDOT in the Orgacon layer is partially positively doped. It appears almost transparent, with a light blue color. Further oxidation of the pristine semi-oxidized polymer makes it slightly more transparent, even though this change is hardly detectable by the human eye and, thus, is not a practically useful electrochromic effect. Reduction of PEDOT⁺ toward the neutral state decreases the number of bi-polaronic states within the band gap and the optical absorption spectrum is shifted from the near infrared region into the visible region, peaking at approximately 640 nm, i.e. PEDOT now absorbs strongly in the visible region, see Figure 17.

![Figure 17](image)

Figure 17. The optical absorption of PEDOT:PSS that shows the electrochromic property. The polymer becomes slightly more transparent upon further oxidation from the pristine semi-oxidized state, while the useful electrochromic switch occurs between the pristine (or oxidized) and the reduced states. The absorption maximum is shifted between the visible region, peaking at 640 nm, and the near infrared region in the reduced and oxidized state, respectively, and can be understood as the result of the significant increase in bi-polaronic states in the oxidized material.
3.2 The electrochromic display cell

The electrochromic display cell bases its operation on the change in optical absorption, see Figure 17, and can be made in either a lateral or vertical device architecture. A lateral electrochromic display cell consists of two adjacent PEDOT:PSS electrodes with a patterned common electrolyte layer placed on top. Once a potential is applied between the electrodes, current can flow in a direction that depends on the polarity of the electrode potentials. The interface between the electrolyte layer and the polymer layer serves as a transducer that converts the current between being electronic and ionic. One of the polymer electrodes is chosen to be the pixel, while the other acts as the counter electrode in the electrochromic display cell. The electrochemical reaction that occurs when a voltage is applied between the two electrodes causes the positively addressed electrode to become further oxidized, while the negatively biased electrode becomes reduced, according to the electrochemical half-reaction:

\[
\text{PEDOT}^+\text{PSS}^- + \text{M}^+ + e^- \leftrightarrow \text{PEDOT}^0 + \text{M}^+\text{PSS}^- \quad (1)
\]

One advantage of using the same material in both electrodes, PEDOT:PSS in this case, is that it ensures low-voltage operation (below 2 V). Equation 1, read from left to right, is a reduction, which is clearly observed as a switch of PEDOT into a semiconducting and deep blue colored state. Oxidation occurs if the half-reaction in Equation 1 proceeds from right to left, which results in higher conductivity and a transition towards transparency. Upon oxidation, the charge of \( \text{PEDOT}^+ \) is balanced by the polyanion \( \text{PSS}^- \) and the electron \( e^- \) and the cation \( \text{M}^+ \) are given up to the polymer film (and eventually the electronic circuit) and the electrolyte, respectively, see Figure 18a. Meanwhile, a reduction process occurs at the other electrode to maintain overall charge neutrality, which requires an electron for the conversion of \( \text{PEDOT}^+ \) to \( \text{PEDOT}^0 \), and the \( \text{PSS}^- \) polyanion binds to a cation \( \text{M}^+ \) provided by the electrolyte instead.

Figure 18a shows the architecture of a lateral electrochromic display cell together with the migration of electrons and ions due to an applied electric potential. This electrochemical process is reversible and the pixel electrode can be cycled between the oxidized, transparent state and the reduced, deep blue-colored state. However, if the process is driven further, either by excessive over-potentials or if a potential is applied during a very long time, the over-
oxidized and irreversible state of PEDOT can be reached, effectively deteriorating the device. Even though over-oxidation is detrimental to electrochemical devices, it can be used as an irreversible patterning method that separates conducting PEDOT:PSS areas in a polymer film by lines consisting of the non-conducting, over-oxidized state of PEDOT:PSS [51].

Figure 18. a) The lateral architecture of an electrochromic display cell is shown, including the migration of electrons and ions that are involved in the electrochemical reaction that occurs when a voltage is applied between the electrodes. b) Photographs of the oxidized, almost transparent, state and the reduced dark blue state of PEDOT:PSS are shown. It should be noted that intermediate gray-scale levels can be achieved by applying a voltage in between the 0.5 and 2 V that is applied here. This particular display cell is vertical and the counter electrode is hidden beneath a whitish electrolyte.

The display cell architecture is to a great extent bi-stable, which means that, once updated the pixel electrode remains in the reduced state when the electric contacts are disconnected, i.e. both the electrodes are potentially left floating. This can be considered as a memory effect, and retention times ranging from a few minutes to several hours has been observed in display cells based on PEDOT:PSS.

There is, of course, a desire to obtain higher optical contrast and to make colors other than the transparent versus dark blue, available in PEDOT:PSS, in electrochromic display cells. This is partly discussed in Paper 4, even though more thorough investigations on the topic of additional colors and improved contrast can be found in the literature [52, 53].
3.3 The electrochemical transistor

Our electrochemical transistor utilize the current switching properties of PEDOT:PSS, i.e. the conductivity of the polymer is switched when the oxidation state of PEDOT is changed. Thus, the electrochemical transistor is a switchable device in which the impedance state of the PEDOT:PSS transistor channel controls the current through the channel. Two different architectures of the electrochemical transistor, that either contains three or four terminals, are briefly discussed below. A switch ratio of \(10^5\) between the on- and off-currents in the transistor channel at an applied gate voltage of either 0V or 2 V, respectively, has been observed and was reported for the four-terminal device [18], while electrochemical logic circuits (inverters, oscillators, NAND- and NOR-gates) have been achieved using the three-terminal device [46].

3.3.1 Three-terminal electrochemical transistor device

A lateral three-terminal electrochemical transistor device consists of a stripe of PEDOT:PSS that defines the transistor channel, and the drain and source electrodes. The gate electrode (also PEDOT:PSS) is positioned adjacent to the channel. The transistor channel and the gate electrode are then ionically, but not electronically, connected by an electrolyte layer deposited on top of the PEDOT:PSS film, see Figure 19.

![Figure 19. Lateral architecture of the electrochemical transistor consisting of the source and drain contacts on either side of the transistor channel. The gate electrode is ionically connected to, but electronically insulated from, the transistor channel by an electrolyte. The area of the electrolyte covering the gate electrode is typically at least 10 times larger than the area of the electrolyte defining the active area in the transistor channel. This allows for full depletion of the transistor channel upon reduction and minimizes the risk of over-oxidation of the pristinely semi-oxidized gate electrode [54]. Since PEDOT:PSS is electrically conducting in the pristine state, the resulting electrochemical transistor operates in depletion mode, that is, a gradual increase of the gate voltage gives a gradual switch towards the non-conducting state of the transistor channel.](image-url)
The electrochemical reaction that occurs when a voltage is applied between the gate electrode and the transistor channel is still represented by Equation 1. This type of transistor operates in the depletion mode since PEDOT:PSS is conducting in its un-biased state (when the gate voltage is 0 V). As a positive voltage is applied to the gate electrode with respect to the transistor channel, further oxidation of the gate electrode and, of more importance, reduction of the transistor channel takes place. Therefore, depending on the value of the applied gate voltage, the conductivity of the transistor channel can be modulated between conducting and semiconducting.

The potential that drives the current through the transistor channel is applied between the drain and source contacts ($V_{DS}$), a potential that causes a second electrochemical switching process to occur inside the channel. The electrical resistance in the conducting state of the transistor channel is on the order of a few kΩ, resulting in a potential drop along the channel due to the applied $V_{DS}$. The active area of the transistor channel is defined by the area of PEDOT:PSS that is covered with an electrolyte layer and, hence, the positively addressed side of the active area in the transistor channel will be further oxidized. In contrast, at the other side of the transistor channel a reductive electrochemical process takes place due to the negatively applied bias voltage. The overall effect can be seen as a doping gradient within the transistor channel that pinches the transistor channel off, which in turn has been observed both in experiments and modeled as a steady-state current generator [55]. The combined effect from the pinch-off and the gate voltage governs the overall current versus voltage (I-V) characteristics in Figure 20.
Figure 20. a) The I-V characteristics of the electrochemical transistor show two current regimes due to the pinch-off effect together with the gate voltage dependence. A pure resistive behavior is observed at low voltages, while the pinch-off gives rise to a saturated current regime at elevated voltages. Increasing the gate voltage from 0 to 2 V results in a gradual decrease of the conductivity in the transistor channel. b) The same data as in a) in a semi-log plot. The current (density) level in the on-state ($V_G = 0$ V) is about 250 µA (250 A/cm$^2$), while the current (density) level is around 50 nA (50 mA/cm$^2$) in the reduced off-state ($V_G = 2$ V), and this results in an on/off-ratio of 5000.

3.3.2 Four-terminal electrochemical transistor device

The idea of the four-terminal transistor device is the same as in the three-terminal device; to modulate the conductivity of the transistor channel by controlling the electrochemical state of the channel via $V_G$-gating. However, the prime difference is that the gate includes a second electrode that is electronically connected to the transistor channel. In Figure 21 the architecture of a laterally configured four-terminal electrochemical transistor device is given. The four-terminal transistor architecture is operated via two different power supplies that are independent of each other, i.e. only connected through the transistor without a common ground, while the three-terminal device is operated with two different power supplies but the gate electrode is referenced to the source contact.
Figure 21. The lateral four-terminal electrochemical transistor is shown. A negatively biased gate electrode that is electronically connected to the transistor channel is added, and the reduction appears in the shape of the letter T. The gate power supply, indicated with filled circles, is disconnected from the potential applied at the open circles between the source and drain electrodes.

In conclusion, an electrochemical smart pixel can be achieved by combining an electrochemical transistor and an electrochromic display cell; a device that takes advantage of both the electronic and the opto-electronic switching properties of PEDOT:PSS. The smart pixel device is further discussed in Paper 1, Paper 2 and Paper 4.
3.4 Electrolytes

The electrolyte layer that is necessary for the electrochemical switching process needs to be confined in order to define the specific active area of an electrochemical device. This is especially important when several devices are monolithically integrated, for example in an electrochemical smart pixel or in an active-matrix display, since the two electrolyte layers used in the transistor and the display cell must remain physically separated in order to prevent leakage currents and undesired electrochemical reactions. This confinement can, for example, be obtained in a patterning step similar to stencil printing, in which the electrolyte layers are defined via deposition through patterned holes distributed along a plastic mask. Various aqueous-based electrolytes have been explored in the development of the electrochemical devices reported herein, partly because they are easily processed and partly because they can be transformed into solidified electrolyte layers after the printing step by evaporating the water at elevated temperature. Poly(sodium 4-styrenesulfonate) (PSS:Na), a polymer that is defined as a polyelectrolyte since it easily dissociates into immobile anionic units (PSS–) and mobile cationic units (Na+) upon solvation in water, has typically been used in combination with sorbitol (gelling agent), glycerol (hygroscopicity) and titanium dioxide (TiO2, opacifier) in the electrochemical devices reported in Paper 1 and Paper 4. However, a liquid electrolyte based on sodium sulfate (Na2SO4) was used in the electrochemical smart pixel characterization presented in Paper 2, to enable easy control of the salt concentration.
3.5 Stretch-alignment of conjugated polymers

Controlling the dichroic ratio, i.e. the orthogonal transmitted optical light intensity divided by the parallel transmitted intensity, through orientated conjugated polymer films has been demonstrated in the past [56-58]. Such chain orientation results in devices that exhibit anisotropic opto-electronic characteristics [59-62]. Recently, it has also been shown that alignment of conjugated polymer chains can be achieved by the force exerted from a shrinking polymer during evaporation. The force is transferred from the shrinking polymer, via an intermediate polymer layer, down to the conjugated polymer in the bottom layer, which results in an intact anisotropic film [63].

The switchable optical polarizer that is presented in Paper 3 is based on electrochromism in stretch-aligned polyaniline, and the lateral display cell setup discussed previously is used to take advantage of the changes in the optical and the electronic properties of this conjugated polymer upon electrochemical switching. Polyaniline switches to the, electrically almost insulating, leucoemeraldine state upon reduction, having a pale white-yellow color. The electrically semiconducting pernigraniline state, obtained through oxidation of the polymer, is dark blue to its color. The resulting device is an optical filter in which the orientation of the polarized absorption is controlled by the applied voltage polarity.

The switchable optical polarizer, which utilizes the combination of electrochromism and the optical polarizing effect that is obtained through stretch-alignment of the polymer, could be used as an active device in order to enhance the contrast in electrochromic display cells or in liquid crystal display applications [60]. Autostereoscopic 3-D representation in volumetric displays as well as multiview displays are other interesting applications in which a tunable optical polarizer could serve as the switchable parallax barrier [64].
3.6 Active matrix addressed displays

There are a large number of electronic consumer products, in which displays are updated via direct addressing [65], on the market today; familiar examples include liquid crystal displays in calculators and digital watches. Such displays typically consist of a certain number of seven-segment characters that are patterned during the manufacturing process. In order to present more complex information in flat panel displays, such as graphics, a technique like matrix addressing has to be used. The general idea behind matrix addressing is that the display cells are distributed in rows and columns to form a matrix, which are updated row by row. Each individual cell, within the entire display matrix, can then be uniquely addressed by applying the updating signals sequentially. The number of electronic connections required in matrix addressing is then the sum of the number of rows and columns, instead of the product of the number of rows and columns, as would be the case for a non-matrix addressed display [66]. The problem with cross-talk might occur in a passively addressed matrix display, since the applied voltage cannot update one unique display cell in the matrix without affecting other display cells, and this results in a reduced contrast as the number of rows and columns are increased. However, addressing algorithms that circumvents this problem have been proposed in, for example, inorganic electrochromic passive matrix addressed displays [67]. In an actively addressed matrix display [68], where an addressing transistor device is connected to each display cell to form a smart pixel, the problem with cross-talk can almost entirely be suppressed. The transistor in the smart pixel is the “active” part since it controls the current to and from the display unit in the matrix.

When such smart pixels are connected to form a cross-point matrix, the transistors can be updated row by row, while the display cells are updated column-wise. By keeping the transistors in the first row conducting (open), while the transistors in the remaining rows are switched to their non-conducting state (closed), the display cells in row 1 can be updated by applying an appropriate voltage at each column. Then, after completing the updating of the first row, the transistors are switched to their closed state and the updating procedure is repeated until the full matrix display has been updated. The role of the transistor is two-fold. First, the transistor retains charges inside “its” updated display cell and, secondly, the transistor suppresses cross-talk in between neighboring addressing lines and columns, see Figure 22.
Figure 22. a) The experimental updating procedure of a 3x3 active-matrix display including the depletion mode electrochemical transistors and electrochromic display cells. The images are organized (0 to 5) according to the update sequence in the c) figure. b) A simple schematic of an active-matrix display is shown: V\textsubscript{COLUMN 1} and V\textsubscript{COLUMN 2} are the display cell update signals, while V\textsubscript{ROW 1} and V\textsubscript{ROW 2} are the voltages connected to the transistor gate electrodes. c) The applied potentials during a full update cycle of the matrix display are shown. (0): The display is initially blank. (1): A gate voltage signal is applied to row 2 and 3, while the transistors in row 1 are kept conducting, and the display cell voltage in the left column line is addressed in order to color the upper pixel to the left. If it were not for the non-conducting transistors in row 2 and 3, the column potential would color all pixels in the left column. (2) The transistors in row 1 are switched to their non-conducting state, in row 2 the transistors are instead switched to their conducting state. The transistor belonging to the previously updated pixel in row 1 now retains the charges inside this display pixel. A potential is applied to the column addressing lines to the left and in the middle and the corresponding pixels in row 2 are updated. (3) The same updating procedure is successively carried out throughout the remaining rows of this small display, i.e. only row 3 in this particular display. (4) After a full update, all transistors are in their non-conducting state and the information is stored in the matrix display, even if a potential of 0 V is applied to the column addressing lines. (5) The information in the display is discharged by an intended short-circuit that allows charge migration to the initial equilibrium state.
To conclude the chapter on electrochemical devices, and to emphasize a few contributions in this thesis, an electrochemical smart pixel can be obtained by combining an electrochemical transistor and an electrochromic display cell; a device that takes advantage of the electrochemically switchable electronic and opto-electronic properties of PEDOT:PSS. The smart pixel device is discussed in Paper 1, Paper 2 and Paper 4 in the thesis. In addition to this, the concept of all-organic electrochromic active-matrix displays printed on paper or plastic substrates have been achieved, and this is further discussed in Paper 1 and Paper 4. In addition to this, a switchable optical polarizer based on the combination of electrochromism and stretch-alignment of polyaniline chains is reported in Paper 3. The resulting device is manufactured according to the electrochemical display cell architecture described above and relies on changes of the opto-electronic properties in a stretch-aligned polymer, which in turn yields control over the orientation of the polarized absorption by the voltage applied.
4 Charge transport modulation in polymer diodes

4.1 Diodes based on organic materials

Organic diodes are constructed according to the architecture of a semiconducting single- or multi-layered stack sandwiched between two conducting electrodes, where the overlap of the electrodes defines the active area of the diode. The work function of the electrodes, the electrode-semiconductor interfaces and the charge transport properties of the semiconductor(s) together predict the overall current density versus voltage (J-V) characteristics of the resulting diode. A lot of research efforts have been dedicated towards understanding the electrical behavior of organic diodes. This has primarily been driven by the need to optimize the electroluminescence properties of organic light emitting diodes [5]. A wide range of organic conjugated materials have been considered as the active semiconductor in the diodes.

Poly[2-methoxy-5(2’-ethylhexyloxy)-1,4phenylenevinylene] (MEH-PPV), which plays a significant role in Paper 5 and Paper 6, is a conjugated polymer that has been extensively investigated as the semiconducting material in organic-based diodes. The architecture of an organic diode together with the chemical structure of MEH-PPV is shown in Figure 23.

![Figure 23. An organic diode is formed when a polymeric semiconductor is sandwiched between two conducting electrodes. The conducting polymer PEDOT:PSS is typically deposited on top of the indium tin oxide (ITO) in order to improve hole injection. The chemical structure of MEH-PPV is shown to the right.](image)
The J-V characteristics of the diode can be measured by applying a potential between the two electrodes. The contacts are considered ohmic when the work functions of the two electrodes are close enough to the HOMO and LUMO energy levels of the semiconducting polymer, respectively, which yields a high probability to achieve rectification in the diode [69, 70]. At reverse voltages, when a negative voltage is applied to the electrode with a work function close to the HOMO level, low current levels are observed since the high energy barriers created prevent charges from being easily injected into the polymer. In the forward direction, at low positive voltages, the current shows ohmic behavior. At increased positive forward voltages, the current increases very steeply and the current shows a space charge (SC) limited behavior. There is, however, another option available when charge traps are present. The current will then be governed by an ohmic behavior until the traps are about to be filled. At that point a transition occurs and the current increases rapidly to eventually, when all traps are filled, saturate into the trap-free SC-limited current regime. Such transitions are typically denoted to occur in the trap-filling regime (TFR) and the current is said to show charge trap (CT) limited current behavior.

For light emitting diodes efficient electron and hole injection is needed. In such devices two different materials are typically used as the electrodes. This results in a built-in potential throughout the semiconductor that, ideally, equals the work function difference between the two electrodes. The importance of taking the built-in potential into consideration during the analysis of the diode J-V characteristics has been reported previously [71]. The built-in potential can, for example, be determined by photovoltaic measurements [72]. Here, the built-in potential forces photogenerated charge carriers to drift through the device. A potential can be applied across the device, which should oppose the drift of the photogenerated carriers. The open circuit voltage is then equal to the applied potential at which the photocurrent approaches zero. To obtain the true built-in potential, this measurement should be performed at low temperature to avoid thermally generated charge carriers.
4.2 Trap-free charge transport in polymer diodes

The J-V characteristic of a diode that is manufactured according to the structure in Figure 23 is shown in Figure 24 below.

![Figure 24](image)

Figure 24. Semi-log and absolute sign plot of the current through a diode wherein MEH-PPV serves as the active material. The current remains low at reverse voltages, i.e. when the ITO electrode is biased in its negative direction and the Al is biased in its positive direction, respectively. The current onset is 1.2 V in this particular diode (the built-in potential is not accounted for), as seen by a rapid evolvement of the current level due to injected charge carriers (hole-mainly). The rectification (between 3-6 V) is three to four orders of magnitude; a value that would increase if the Al is changed to a low work function cathode.

In the ohmic region (below 1.2 V in Figure 24) the current density is directly proportional to the applied electric field \( J \propto \frac{V}{d} \), which would result in a slope \( m = 1 \) in a log(J)-log(V)-plot. At higher applied voltages, when the injected charge carriers build up space charge due to the low mobility in the semiconducting polymer, the transported charges follow SC-limited current behavior. Assuming that the transport can be considered trap-free, which often is the case in polymer diodes where mainly holes are present [69], the J-V curve should obey the Mott-Gurney equation [73]:

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_p \frac{V^2}{d^3}
\]

(2)
Here, \( \varepsilon_0 \) and \( \varepsilon_r \) is the vacuum permittivity and the relative material permittivity, respectively, and \( \mu_p \) is the hole mobility. Since \( J \propto \frac{V^2}{d^3} \) in Equation 2, the log(J)-log(V)-plot evolves with a slope \( m = 2 \). The current also shows stronger thickness dependence as compared to the ohmic regime. The Mott-Gurney equation assumes that the mobility remains constant throughout the entire voltage region, which is not particularly true in a disordered polymer diode. Another prediction that successfully has been used to treat the field-dependent mobility in the high voltage regime is the Murgatroyd SC-limited current model [71].
4.3 Trap-limited charge transport in polymer diodes

Imperfections and disorder in crystalline or semi-crystalline semiconducting materials are generally caused by structural defects and/or impurities. These defects cause energy levels to be introduced within the energy gap of the semiconductor. These energy levels serve as localized states which often are called charge traps or recombination centers. The density of charge traps, typically denoted \( H_t \) and measured as the number of charge traps per unit volume, in a semiconducting material has strong impact on the \( J-V \) characteristics in electronic devices. Each charge trap is positioned at a certain “depth” inside the band gap of the semiconductor. The charge traps may occur at a specific energy level in the case of a single crystal, while they are considered to be distributed in energy in polycrystalline or amorphous materials, such as polymers. The trap density as well as the characteristic charge trap energy can differ within the material, which strongly affects the \( J-V \) characteristics in a device. The characteristic charge trap energy is a measure on how the traps are distributed in energy (\( E_t \) [eV]), often expressed as the characteristic charge trap temperature (\( T_t \) [K]) instead.

The most simple system for studying trap-limited conduction is a material where the charge traps are confined in single, or multiple, discrete energy level(s). The current in such systems is predicted by the modified Mott-Gurney equation:

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_p \theta \frac{V^2}{d} \tag{3}
\]

Holes are assumed to be the dominating charge carrier and the ratio between free and trapped holes is denoted by:

\[
\theta = \frac{p}{p + p_t} \tag{4}
\]

The current increases according to the modified Mott-Gurney equation as the applied voltage across the device increases. At a certain voltage, the quasi-Fermi level will pass the energy at which the charge traps are located. This results in that the traps are filled and, hence, this critical voltage is denoted the trap filled limit (TFL) voltage. Increasing the voltage across the
device further results in more injected charge carriers, but these carriers are considered free since the traps are already filled. This, in turn, results in a rapid transition of the current level towards the trap free SC-limited conduction regime.

Ideally, the charge traps could be separated in several distinguishable charge trap energy levels. This would be seen in the J-V curves by several rapid transitions; one for each discrete trap energy depth.

The transition from ohmic to SC-limited conduction obeys the following equation:

$$V_{onset} = \frac{8qP_xd^2}{9e_0E_0\theta}$$  \hspace{1cm} (5)

Thus, the charge trap density clearly influences $V_{onset}$. High charge trap density yields high $V_{onset}$. However, it should also be noted that a very high charge trap density within the material might result in Poole-Frenkel emission, that is, trapped charge carriers are transported by hopping between neighboring impurity sites under the influence of an electric field or by thermal activation. This phenomenon, which gives rise to a current contribution due to the charge traps, is more pronounced at low temperatures due to low thermal detrapping probability. Furthermore, this is also thought to be the mechanism observed in a device reported by Tsujioka et al. [24]. Here the device, which contains an active photochromic layer, exhibits a dramatic increase of the current throughput due to hole hopping between the increased number of trapping sites after exposure to UV light.

The energy at which the traps are located is typically denoted as shallow or deep, see schematic in Figure 25. Shallow traps are defined by a trap depth of $E_t < E_{Fp0}$, where $E_{Fp0}$ is the quasi-Fermi energy level in the absence of an applied voltage, and they typically show high probability of thermal trap emptying and/or trap emptying due to the applied electric field. In this case, there will first be a transition from the ohmic conduction to the trap-limited behavior in which the traps are gradually filled, and when all traps eventually are filled the current evolves towards the trap free SC-limited current level above the TFL voltage. Furthermore, the TFL is shifted to a higher voltage when the charge trap density is increased.
Deep traps are, instead, defined by a trap depth of $E_t > E_{Fp0}$. The behavior of the current evolution as a function of the applied voltage differs when the traps are considered to be energetically deep inside the band gap of the semiconductor. Here, all injected charge carriers are used for trap filling and, therefore, the TFL voltage is defined as a transition from ohmic conduction directly to the SCLC level. The gradual trap filling that occurs for shallow charge traps would not be observed in this case. The TFL voltage is, however, still proportional to the charge trap density.
4.4 Charge trap distributions

The trap-limited charge transport described above assumed that charge traps are single or multiple discrete energy levels below the transport level. This is, however, nearly never the case in polymer diodes due to the presence of electric dipole induced energy disorder. Instead, the charge trap states have various energies described by a distribution within the band gap of the semiconductor. Two different charge trap distribution functions have been used by various authors to describe their experimental data: the exponential and the Gaussian charge trap distributions.

The exponential charge trap distribution is mathematically straightforward to use, as compared to the Gaussian distribution, and does not require knowledge about the energetic position of the average trap energy. Although less general, since that the model might not be relevant for deep traps, the exponential distribution provides comparable results to those obtained by the Gaussian model [74]. For these reasons, the exponential charge trap distribution has been extensively used and will be used here again in the analysis provided in Paper 5.

In the following, several approximations will be used: (i) the charge carrier (e.g. hole) transport takes place in a well-defined frontier energy level of the organic semiconductor (e.g. HOMO in Figure 26). Hence, the energy disorder present in polymers, and typically modeled by a Gaussian energy distribution of HOMO levels, is neglected. The charge traps are distributed below this discrete level according to an exponential function; thus reducing the number of free charge carriers contributing to the current density. Upon increasing the applied voltage between the electrodes of the diode, the charge carrier density increases, such that the quasi-Fermi level moves in the exponential trap distribution towards the HOMO level. At low voltage, the charge carriers are trapped and the current is low. An increase of electric field leads to a filling of those trap states until the quasi-Fermi level reaches the high density of states region of the exponential distribution, i.e. close to the HOMO level of the polymer. A further increase in charge carrier density at higher voltage results in the occupation of the transport level of the semiconductor (e.g. the HOMO level), where charge carriers have high mobility. Hence, the current rapidly rises up towards trap-free SC-limited current.
Besides the exponential energy distribution of the traps described by Equation 6, the spatial charge trap distribution is assumed to be uniform between the two electrodes ($s(x) = 1$): \[
H(E) = \frac{H_t}{E_t} \exp\left(-\frac{E}{E_t}\right)
\] (6)

$H(E)$ is the (hole) charge trap density at a certain energy $E$ beyond the (valence) band edge, $H_t$ is the total trap density, $E_t$ is a parameter defining the trap energy distribution, the ratio $H_t/E_t$ denotes the trap density at the (valence) band edge. The maximum number of charge traps is located at the valence band edge, while the trap density decreases exponentially as the trapping sites are positioned deeper inside the band gap of the semiconductor. $E_t = kT_t$ and $l = T_t/T$, where $l$ can be experimentally determined from the slope of the log-log plot of the J-V characteristics in the trap filling regime. Indeed, the current throughput obeys a $J-V^m$ power-law (see Equation 8 below) such that $m = l+1$ is the slope in the log(J)-log(V) plot. In order for the exponential distribution to be in reasonable agreement with a Gaussian distribution model, the value of $l$ should be constant over a rather large voltage range. $l$ should also remain constant when the dependence of the thickness on the current density is investigated. The essential experimental parameter to vary when investigating charge trapping is the temperature dependence of the slope since $E_t$ equals $kT_t$ in Equation 6.
Figure 26. Sketch of the exponential and Gaussian distribution of hole traps in the vicinity of the valence band edge (HOMO level) of the organic semiconductor. The Gaussian function has its average energy close to the HOMO level. The exponential distribution has its maximum number of trapping sites close to the HOMO level, and the trap density then decays exponentially towards the deeper positioned charge traps.

The Gaussian trap distribution is given by Equation 7 and is sketched with the exponential distribution in Figure 26. $H(E)$ is the charge trap density at a certain energy $E$, $H_t$ is the total trap density, $E_{max}$ is the energy of the trap level at the maximum density of trap states (or average) defined as an energy difference from the HOMO energy level. $\sigma$ is the standard deviation of the Gaussian distribution. $E_F$ denotes the quasi-Fermi level that moves from the deepest trapping level towards the HOMO level under influence of an applied electric field.

$$H(E) = \frac{H_t}{\sqrt{2\pi\sigma^2}} \exp(-\frac{(E - E_{max})^2}{2\sigma^2})$$  \hspace{1cm} (7)

In Figure 26, $\Delta E$ represents a typical energy region (~0.3 eV) in which the quasi-Fermi level is swept in a diode measurement. In that region, the density of trap states are fairly similar for the two charge trap distributions discussed [74]. Hence, the exponential model is likely a reasonable model to interpret the J-V characteristics of polymer diodes.
4.5 The exponential charge trap distribution

An extension of the exponential charge trap distribution is used in Paper 5 to determine the charge trap density. The analysis is based on the work by Kumar et al. [75], who give a straightforward extraction of the charge trap density from the J-V curves recorded at various temperatures. In the trap-filling regime (TFR), the current density evolves according to a power-law behavior given by Equation 8 [76]. In a log-log graph, the slope of the J-V curve is steeper than the space charge limited current between the critical potential at which the first transition occurs \( (V_C) \) and the trap-free SC-limited regime.

\[
J = q^{-\epsilon_i^2} \mu_p N_v \left( \frac{2l+1}{l+1} \right)^{\epsilon_i} \left( \frac{l}{l+1} \right)^{\frac{\epsilon_i}{\epsilon_0}} V^{l+1} \frac{d^2}{2^{l+1}} \]

where \( \epsilon_i \) and \( \epsilon_0 \) are the dielectric constant and the vacuum permittivity, respectively. \( d \) is the sample thickness, \( q \) is the elementary charge, \( \mu_p \) is the charge carrier mobility, \( N_v \) is the density of states, \( V \) is the applied voltage and \( T \) the temperature. As mentioned previously, in the TFR, the slope of the J-V characteristic on log-log scale determines the characteristic temperature \( T_t \), but it does not reveal any information regarding the charge trap density. The trap density can be estimated by using the temperature dependence of the Arrhenius form of Equation 8 [75, 77]:

\[
J = \left( \frac{q \mu_p N_v}{d} \right) f(l) \exp \left[ -\frac{E_i}{kT} \ln \left( \frac{qH d^2}{\epsilon_i \epsilon_0 V} \right) \right],
\]

where \( f(l) = \left( \frac{2l+1}{l+1} \right)^{\epsilon_i} \left( \frac{l}{l+1} \right)^{\frac{\epsilon_i}{\epsilon_0}} \)

\[
\frac{1}{2^l} \text{ is introduced to make } f(l) \approx \frac{1}{2} \pm 4\% \text{ for } l > 2, \text{ which gives the modified } f(l):
\]

\[
f(l) = \left( \frac{2l+1}{l+1} \right)^{\epsilon_i} \left( \frac{l}{l+1} \right)^{\frac{\epsilon_i}{\epsilon_0}} \frac{1}{2^l}
\]
The advantage of this manipulation is that \( f(l) \), within ± 4% margin of error, equals 0.5 for all \( l > 2 \). Experimental device data typically show values of \( T_t \) between 1000 and 1500 K, at least, which results in \( l \geq 3.5 \). Therefore, by treating \( f(l) \) as a constant (equal to 0.5), Equation 9 becomes:

\[
J = \left( \frac{\mu_r N_s q V}{2d} \right) \exp \left[ \frac{E_t}{kT} \ln \left( \frac{qH_s d^2}{2e_0 \epsilon V} \right) \right]
\]

(12)

This results in that the trap density can be determined from an Arrhenius plot, that is, \( \log(J) \) versus \( 1/T \) (Figure 27a). The slope in this graph gives the activation energy determined by Equation 13. In Figure 27a, the activation energy becomes smaller as the applied voltage is increased. Finally, when the applied voltage equals \( V_X \), the simulated device shows no dependence on temperature. Once \( T_t \) is estimated from the log-log slope of the J-V characteristics at one or several temperatures, the remaining factors in Equation 13 are known and the trap density \( H_t \) can easily be calculated.

\[
E_x = E_t \ln \left( \frac{qH_s d^2}{2e_0 \epsilon V} \right)
\]

(13)

The other method to determine the trap density is to identify the potential at which the current density is independent on temperature, which defines the cross-over voltage (\( V_X \)), see Figure 27b. At the measured \( V_X \), the activation energy equals zero and the trap density is directly given by:

\[
H_t = \frac{V_s 2e_0 \epsilon}{qd^2}
\]

(14)
The $V_X$ cross-over voltage is observed at elevated applied potentials, typically exceeding the possible measurement range of a polymer diode. Therefore, $V_X$ is determined from linear extrapolation of the data points following the power-law behavior within the TFR. The method of extrapolation to find the intersection, here denoted $V_X$, for elevated voltages at which the $J$-$V$ data points are independent of temperature, was performed on the diodes containing switchable charge traps in order to determine the change in charge trap density, see Paper 5.

One of the results from the temperature data presented in Paper 5 is that, on average, the number of charge traps is doubled after exposure to UV wavelengths. From Equation 12 it can be seen that the current density scales according to Equation 15, and by insertion of the $T_t$ value obtained in Paper 5 the following scaling of the current density is found:

$$J \propto H_t^{-1} = H \frac{T}{T_t} = 2 \frac{1450}{791} \approx \frac{1}{30}$$

The value of the current density is reduced by a factor of 30 when the charge trap density is doubled, and this value is in agreement with the current density switching factor that is obtained in diodes consisting of this particular fraction of PC guest molecules blended into the semiconducting MEH-PPV polymer host.
It is possible that the Gaussian charge trap distribution would be a more appropriate model to describe charge transport for diodes including PC guest molecules in a semiconducting polymer host. This is due to the fact that the low energy gap state of a certain PC molecule is thought to function as a charge trap with a particular trap depth inside the band gap of the semi-conducting polymer, suggesting that the behavior of an exponential charge trap distribution does not give a valid picture of the system. Having the illustration of Figure 26 in mind, the parameters of a Gaussian distribution can be chosen such that the maximum of the distribution is located at a specific charge trap energy inside the gap. This trap energy should of course equal that of the HOMO energy level of the PC molecule in its low energy gap state. However, the HOMO level of the PC molecule used in Paper 5 and Paper 6 has not yet been revealed. Recently, several publications have reported appropriate modeling of guest-host systems taking the mobility dependence of the charge carrier concentration into account as well as that the density of states dispersion is described with dual Gaussian peaks; one peak governs the disorder of the polymer host and the other peak predicts the guests (charge traps) that are located inside the semiconductor band gap [78-84]. Such model would be interesting to apply to diodes that contain a solid-state blend of a conjugated polymer and a PC molecule.

To conclude this chapter on charge transport modulation in polymer diodes, and to emphasize the scientific contributions that are included in Paper 5 and Paper 6; an organic electronic device based on a solid-state blend of a conjugated polymer and a photochromic molecule has been manufactured and studied. This blend, sandwiched between two electrodes, results in a polymer diode that can, upon light irradiation, reversibly be switched between two different states, which exhibit distinctly different charge transport characteristics. The suggested model to describe the switch mechanism is that the PC molecular switch traps holes, as it is switched to its low energy gap state. This is then reflected in that the current is lowered through the diode due to that the charge transport switches from SC-limited to CT-limited conduction. The device is sensitive to the dose of absorbed (UV) light and this “gray-scale” feature can be read out by measuring the current through the diode. The device can therefore be used as the UV light detector in passive matrices in, for example, detector and imaging applications. Besides this, the in situ switching of the charge trap density provides a nice tool to study the charge transport characteristics of organic materials.
5 Conclusions

The contributions that are reported in Papers 1 to 4 relate to optical absorption switching in electrochromic display cells and charge transport modulation in electrochemical transistors. By combining the electrochemical transistor with the electrochromic display cell results in an electrochemical smart pixel device, in which the transistor controls and addresses the updating current for the display cell. Smart pixels can then be arranged in cross-point matrices to form an active matrix addressed display wherein desired information content can be presented by the appropriate updating procedure. The resulting all-organic electrochromic active-matrix display can be manufactured on a flexible substrate, such as paper or plastic foil, by using common printing tools. This technology is, therefore, one of several available pathways in the attempts of achieving an electronic paper technology; a technology that mimics the appearance of ordinary paper but with updateable information content [85]. Even though this technology cannot compete with already existing display technologies in terms of updating speed, it shows several other strong advantages:

- Low voltage operation makes direct incorporation of printable batteries in the active-matrix displays feasible
- Soluble, all-organic materials allow for manufacturing of flexible active-matrix displays on either paper or plastic substrates
- The electronic property of PEDOT:PSS is used in both the electrochemical transistors and in the conducting lines, while the optical property is used in the electrochromic display cells. Thus, only one active material is required in the active-matrix displays
- Recent developments have resulted in a simplified display design that possibly could enable reel-to-reel manufacturing of active-matrix displays since neither additional resistors nor electrical vias are required
- Updating schemes, color contrast and fill factor are other important issues that have been addressed recently

However, it should also be noted that the most significant disadvantage of the active-matrix display system is the combination of the depletion mode transistor and the ionic conductivity in PEDOT:PSS, as mentioned in Paper 4. The reason for this is that the voltage strain on the transistor channel might cause a reduction front [86] to propagate outside the electrolyte confinement of the transistor channel, and this is detrimental to the switching time of the
transistor. The most straightforward choice to circumvent this problem would be to use a transistor that is operating in enhancement mode.

The contributions included in Paper 5 and Paper 6 relate to charge transport modulation in a polymer diode where *in situ* photo-initiated switching of the charge trap density is demonstrated. The active diode layer is based on a blend of a semiconducting polymer host and PC molecules. The state of the PC molecule determines whether the holes that are transported through the diode are governed by SC- or CT-limitation. The proposed mechanism behind this phenomenon is that the HOMO level of the PC molecule serves as a charge trap when it is switched inside the band gap of the polymer semiconductor upon UV light irradiation. The process is then reversed, i.e. traps are switched out from band gap of the host, by exposure to visible light. Another approach to actively control the current through a diode with PC molecules was suggested by Tsujioka *et al*. In their work the PC molecules functioned as the switchable charge injection barrier [23, 24, 87-90]. However, the groups of Nespurek and Sworakowski suggest another approach and model that takes the dipole moment of the PC molecules into account [25, 39, 91, 92]. Switching PC molecules from the high to the low energy gap state by UV light exposure will, in most cases, result in an increased dipole moment, which in turn reduces the current through the diode due to broadening of the Gaussian transport distribution. Based on this, one can conclude that more research efforts are required in order to fully understand the combination of conjugated polymers and PC molecular switches explored in organic electronic devices.
6 References

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