Surface Energy Patterning and Optoelectronic Devices Based on Conjugated Polymers

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Cover figures:

*Picture on the left:* Microscope image of polymer patterns formed directly from solution by surface energy controlled dewetting.

*Picture on the right:* Photon to current efficiency curves of solar cells based on a novel low-bandgap polymer blended with different fullerenes.
To Lichun and Gengshi
Abstract

The work presented in this thesis concerns surface energy modification and patterning of the surfaces of conjugated polymers. Goniometry and Wilhelmy Balance techniques were used to evaluate the surface energy or wettability of a polymer’s surface; infrared reflection-absorption spectroscopy (IRAS) was used to analyse the residuals on the surface as modified by a bare elastomeric stamp poly(dimethylsiloxane) (PDMS). The stamp was found to be capable of modifying a polymer surface. Patterning of a single and/or double layer of conjugated polymers on the surface can be achieved by surface energy controlled dewetting. Modification of a conjugated polymer film can also be carried out when a sample is subjected to electrochemical doping in an aqueous electrolyte. The dynamic surface energy changes during the process were monitored in-situ using the Wilhelmy balance method.

This thesis also concerns studies of conjugated polymer-based optoelectronics, including light-emitting diodes (PLEDs), that generate light by injecting charge into the active polymer layer, and solar cells (PSCs), that create electrical power by absorbing and then converting solar photons into electron/hole pairs. A phosphorescent metal complex was doped into polythiophene to fabricate PLEDs. The energy transfer from the host polymer to the guest phosphorescent metal (iridium and platinum) complex was studied using photoluminescence and electroluminescence measurements performed at room temperature and at liquid nitrogen temperature. PSCs were prepared using low-bandgap polyfluorene copolymers as an electron donor blended with several fullerene derivatives acting as electron acceptors. Energetic match is the main issue affecting efficient charge transfer at the interface between the polymers and the fullerene derivatives, and therefore the performance of the PSCs. Photoluminescence, luminescence quenching and the lowest unoccupied molecular orbital (LUMO) together with the highest occupied molecular orbital
(HOMO) of the active materials in the devices were studied. A newly synthesized fullerene, that could match the low-bandgap polymers, was selected and used as electron acceptor in the PSCs. Photovoltaic properties of these PSCs were characterised, demonstrating one of the most efficient polymer:fullerene SCs that generate photocurrent at 1 µm.
Preface

This work has been performed in the Biomolecular and Organic Electronics group in the Division of Applied Physics, at the Department of Physics, Chemistry and Biology at Linköping University, Sweden. I enrolled as a Ph D student under the supervision of Prof. Olle Ingañas in the research project “From nano-scale interactions to optoelectronic devices of conjugated polymers” in The National Network Research School in Materials Science, supported by the Swedish Education Ministry since March 2002 after I had been a project engineer for more than a year in the same group. The project has been performed with the cooperation of four Ph D students with backgrounds in theoretical physics, conjugated polymer synthesis and surface characterization and device physics applications from Chalmers University of Technology, Karlstad University and Linköping University.

The work presented in this thesis concerns surface energy modification and patterning of surfaces of conjugated polymers; and studies of conjugated polymer-based optoelectronics, including light-emitting diodes (PLEDs), that generate light by injecting a charge into the active polymer layer, and solar cells (PSCs), that create electrical power by absorbing and then converting solar photons into electrons.

Xiangjun Wang, Linköping, Sweden, December 2005
List of publications:

Papers included in this thesis:


III. X. Wang, T. Ederth, and O. Inganäs, In-situ Wilhelmy balance surface energy determination of poly(3-hexylthiophene) and poly(3,4-ethylenedioxythiophene) during electrochemical doping-dedoping. *In manuscript.*


VII. X. Wang, E. Perzon, W. Mammo, F. Oswald, S. Admassie, N.-K. Persson, F. Langa, M.R. Andersson, and O. Inganäs, Polymer solar cells with low-bandgap polymers blended with C$_{70}$-derivative give photocurrent at 1 µm. *Thin Solid Films,* (Accepted for publication).
My contribution to the above papers:

<table>
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<tr>
<th>Paper</th>
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<th>Writing</th>
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<td>VI</td>
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<td>First version (80%)</td>
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<td>VII</td>
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<td>First version (80%)</td>
</tr>
</tbody>
</table>

Related publications, not included in the thesis:


Conference contributions:


Acknowledgement

Four-years of Ph D study and research are approaching an end. It is time to express my sincere gratitude to the people who make my Ph D work fruitful and my life enjoyable.

I have been very fortunate to get the opportunity to be a project engineer (for short time) and then subsequently be recruited as a Ph D student working in Biomolecular and Organic Electronics at the division of Applied Physics, in the Department of Physics, Chemistry and Biology at Linköping University, Sweden. The group is filled with very active and positive people; the atmosphere was extraordinary for conducting multidisciplinary research. The experience has allowed me to develop my abilities in scientific research and management. Thank must go first to my supervisor, Prof. Olle Inganäs, for his creative ideas, continuous encouragement and patient guidance in my hunt for new insights and understanding behind the phenomena of my studies.

I would also like to gratefully acknowledge Magnus Krogh who introduced the fantastic soft lithography technique to me and helped me initially in my work for the European “Highlight Project”. His experience and knowledge were invaluable for making the project go smoothly.

Thanks also go to Dr Mattias Östblom for his IRAS measurements, giving clear interpretation of the PDMS stamp modification effect and for general discussions. Furthermore, Dr Thomas Ederth was more than helpful in sharing his knowledge on characterizing surface energies using a Wilhelmy Balance.

Prof. Mark E. Thompson at University of California supplied his phosphorescent dyes for us to use and his kind suggestions and revision of my manuscript for Paper III, thank you very much.

I am grateful to Erik Perzon, Lars Lindgren, Prof. Mats R Andersson and their colleagues at Chalmers University of Technology synthesizing novel low- and high-bandgap polyfluorene copolymers and many years cooperation and
also to people: Juan Luis Delgado, Pilar de la Cruz and Prof Fernando Langa, in Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, Spain, synthesizing the fullerene derivatives. The solar cells prepared in Linköping showing some of the best results in this field result from the efforts. The help obtained made it possible for us to investigate device physics in such polymer-fullerene bulk heterojunction solar cells.

I am also indebted to interactions with some of the previous and almost all the current members of the Biomolecule and Organic Electronics Group, in the form of performing experiments together and ending with writing a paper. Also reviewing papers within the internal referee system, being an assistant in the lab and having fruitful discussions on previous and ongoing projects, had a huge impact on my achievements and are very appreciated. I learn a lot of from all of you.

I am grateful for the financial support from the National Graduate School in Material Science and to all the people with whom I cooperated within the network project: Erik Perzon, Mats Andersson, Cecilia Björström, Ellen Moons, Kjell Magnusson, Fengling Zhang and Olle Inganäs. The meetings and communications were also important.

Discussion with or help from people in Prof. Magnus Berggren’s group of Organic Electronics in Norrköping Campus are also appreciated.

Thanks to Dr Stefan Welin Klintström for his useful suggestions and reminders. Thanks also to our secretary Ann-Marie Holm for managing trips and taking care of documents for group members.

Thanks also go to Dr David Lawrence. With your contribution and effort, the thesis presents my PhD work in a much nicer way.

Thanks to technicians Bo Thuner and Wim Bouwens for their support.

I am also grateful to friends in China, Sweden and everywhere over the world for their support and concern.
Love, support and understanding from my husband, Dr Lichun Chen, and my daughter, Gengshi, have been extremely important during the years. I express my deep gratitude to you both. I wish I could present my love to you two and be an excellent wife and a mother, in return, for all of our future years.

/Xiangjun Wang
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1. General introduction

Conjugated polymers have attracted considerable interest since the first conjugated-polymer-based light emitting diodes (LEDs) were created in 1990\(^1\). Polymers belonging to the conjugated polymer family are capable of acting as conducting or semiconducting materials and are used in polymer-based optoelectronics devices, such as light emitting diodes, photovoltaic solar cells, field effect transistors, lasing devices and actuators\(^1\)-\(^5\). These devices usually contain several conjugated polymer layers that are prepared from an organic solution of the polymers. For certain reasons, for instance when fabricating addressable polymer LEDs for a display, or when optimising optical or electric behaviour in an optoelectronical device when light propagates through the device, the film of the polymers is required to be patterned\(^3\)-\(^5\)-\(^7\). Characterization of the surface energy of a conjugated polymer gives information about the surface wettability and the interaction between the surface and a surrounding liquid. This characterization is important for understanding film formation and therefore for optimisation of these devices. Surface energy modification can be used for changing the surface wettability. This may result in a modified surface with a desirable alternating decreased and increased wettability region.

In this thesis, a brief review of the concept of conjugated polymers and their properties is given in Chapter 2. Chapter 3 describes the characterization of the surface energy of conjugated polymers using the Goniometry and Wilhemy Balance methods. This is one of the major parts of the work presented in the thesis. In particular, the novel method of surface modification using a bare elastomeric stamp made from poly(dimethylsiloxane) (PDMS), is presented for the first time. Soft lithography for the patterning of polymers is described in Chapter 4. A method, for patterning of polymers on PDMS modified surfaces with surface energy controlled dewetting, is developed.
In chapter 5, the preparation and characterization of conjugated-polymer-based optoelectronics devices, including LEDs, that generate light through the injection of charge into the active polymer layer, and solar cells (SCs) that create electric power by absorbing solar photons and converting them into current, are presented. Phosphorescent metal complexes were doped into polythiophene to fabricate LEDs. Energy transfer from the host (the polymer) to the guest (the phosphorescent metal (iridium and platinum) complex) was studied using photoluminescence and electroluminescence measurements performed at room temperature and at liquid nitrogen temperature. Solar cells were fabricated using low-bandgap polyfluorene copolymers as electron donors blended with several fullerene derivatives as electron acceptors. Luminescence quenching measured by photoluminescence and the lowest unoccupied molecular orbital (LUMO) along with the highest occupied molecular orbital (HOMO) of the active materials, measured using cyclic voltammograms, were used to discuss the energetic match for efficient charge transfer at the interface between the polymers and the fullerene derivatives. Newly synthesized fullerenes that could match the low-bandgap polymers were selected and used as electron acceptor for preparing SCs. Photovoltaic properties of these SCs were characterised, demonstrating that one of the most efficient polymer:fulleren SCs that generates photon current at 1 µm was obtained.
2. Conjugated polymers

2.1 Chemical configuration and electronic structure

A conjugated polymer is a kind of macromolecule that consists of alternating single and double carbon-carbon bonds in the main chain (backbone), as illustrated in Fig. 2.1. These bonds are constructed of three $sp^2$ and one $p_z$ orbitals that are hybridized from the $2s$ and $2p$ electrons of the carbon atom (see Fig. 2.1). The three $sp^2$-orbitals form a $\sigma$-bond that lies in a plane, with each orbital crossing the others at a common point with an angle of 120°. The electrons are strongly localized. The $p_z$ orbitals overlap each other and form a $\pi$-bond, intersecting through the center of a $\sigma$-bond at an angle perpendicular to the plane of the $\sigma$-bond. The electron in the $\pi$-bond can be mobile over several carbon atoms and is not as localized as the electron in the $\sigma$-bond. The distance the electrons are allowed to travel within the same chain is referred to as the conjugation length. $N$ delocalized electrons occupy $N/2$ molecular orbitals and all molecular orbitals are split into two groups: occupied ($\pi$) and unoccupied ($\pi^*$). Thereby an energy band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is formed and stabilization of the electronic structure is achieved. The band gap is proportional to the reciprocal of the conjugation length $^{8-10}$.

Chemical configuration and electronic structure allow the conjugated polymer to have desirable properties for a wide variety of applications in optoelectronics and sensors.

The chemical structures of some of the conjugated polymers that are historically important, or the concern of this thesis, are shown in Fig. 2.2.
Fig. 2.1. The configurations of conjugated polymers. (1) The 2s- and 2p-orbitals of carbon atoms are hybridised to sp$^2$ and p$_z$-orbitals. (2) σ-bones (above) and π-bond (below) construction in conjugated polymers. (3) The chemical structure of a conjugated polymer poly(acetylene).
Fig. 2.2. The chemical structures of polymers those are important or studied in this thesis. (1) The first, synthesized, conducting polymer, discovered by S. Shirakawa and his coworkers who were awarded the Nobel Prize in 2000\textsuperscript{11-13}. (2) The first polymeric light emitting diode made from poly(para-phenylene-vinylene) by a spin-coating technique\textsuperscript{1}. Polymers from (3) - (6) are semiconductors and their derivatives are often used in polymer opto- or electronics.

2.2 Optical absorption and emission

A conjugated polymer can undergo a transition of its electronic state from the ground to an excited state (i.e. to an exciton) or from an excited to the ground state \emph{via} the absorption or emission of photons. Only singlet-singlet transition can be induced under optical excitation, according to the spin-conservation rule. Optical transition between vibronic energy levels in a conjugated polymer is shown in Fig. 2.3.
**Fig. 2.3.** Optical transitions between vibronic energy levels in a conjugated polymer.

2.3 *Electroluminescence*

When a semiconductor material, for instance a polymer film, is under the influence of an electric field, electrons may be injected into the conduction
band and a hole in the valence band and thereby an exciton is induced. Recombination of an electron and hole pair can lead to the emission of photons. This is referred to as electroluminescence. Contrary to optical excitation, both the singlet and triplet states can be electrically excited. Only the transition of a singlet-ground state is allowed and generates light. That of a triplet-ground state is spin forbidden, implying that only one quarter of the available excitons can be internally converted into light. The remainder of the electric power is lost. However, the triplet-ground transition might be utilized to generate light, by doping heavy metal complexes into polymers, enhancing the electricity-to-light conversion efficiency. Details on how to utilize triplet exciton will be discussed in section 5.2.

2.4 Exciton decay routes and dissociation

In addition to the radiative decay of an exciton (from the excited state to the ground state) that gives off photon emission, there are other ways to relax the excited state (see Fig. 2.4):

a. Internal conversion (IC): relaxation progresses from higher to lower singlet or from higher to lower triplet state through a non-radiative decay which gives off energy in the form of torsional and vibrational quanta.

b. Inter system crossing (ISC): relaxation goes from the lowest singlet to the lowest triplet or from the lowest triplet to lowest singlet state.

The IC process is common in conjugated polymers because the density of the vibration levels increases the probability. ISC is important for a molecule that contains a heavy atom, because of spin-orbital coupling. Polythiophenes contain heavy sulphur atoms and make the ISC yield as high as 40%.

In addition, the excitons formed through the absorption of photons can also be dissociated into a separate electron and hole. For this to happen a higher affinity molecule must be available and be located close to the polymer. An electron can then be transferred to the high affinity molecule. Collection of
these electrons from the secondary molecule onto an electrode gives a photoinduced current. This is the basis for photovoltaic or solar cells. Details about current generation induced by absorption of photons will be described in section 5.3.

Fig. 2.4. Different transition and excitation decay routes in a conjugated polymer molecule.

2.5 From insulator and semiconductor to metal

Conjugated polymers, in pristine and neutral states, are insulators with wide band gap or semiconductors with narrow band gap. The energy band gap of the semiconducting conjugated polymer is normally in the range from 1 to 4 eV, which is similar to that existing in the common inorganic semiconductor. Conjugated polymers may have metallic properties, i.e. high conductivity, after the neutral polymers undergo reduction (n-doping) or oxidation (p-doping) by withdrawing or adding electrons or ions, where a deformation of the main chain is introduced. This is referred to as doping a polymer. A charged polymer molecule, if it creates a degenerate state within the band gap, forms a soliton, such that the conductivity of the polymer is increased. The conductivity of conjugated polymers can cover the range from insulator ($10^{-10}$ S/m) to metal ($10^7$ S/m)$^{17}$. Charged polymer molecules can also generate non-degenerate electronic states in the band gap, forming polarons or bipolarons, such that the
optical properties of the polymer are modified\textsuperscript{18-20}. Fig. 2.5 shows the chemical, and electronic structures of a polaron and a bipolaron and their charge and spin.

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Electronic structure</th>
<th>Charge and spin</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical structure" /></td>
<td><img src="image2" alt="Electronic structure" /></td>
<td>CB: 0 and 0, Neutral state</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical structure" /></td>
<td><img src="image4" alt="Electronic structure" /></td>
<td>CB: +e and 1/2, Positive polaron</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical structure" /></td>
<td><img src="image6" alt="Electronic structure" /></td>
<td>CB: +2e and 0, Positive bipolaron</td>
</tr>
<tr>
<td><img src="image7" alt="Chemical structure" /></td>
<td><img src="image8" alt="Electronic structure" /></td>
<td>CB: -e and 1/2, Negative polaron</td>
</tr>
<tr>
<td><img src="image9" alt="Chemical structure" /></td>
<td><img src="image10" alt="Electronic structure" /></td>
<td>CB: -2e and 0, Negative bipolaron</td>
</tr>
</tbody>
</table>

**Fig. 2.5.** Four new levels are introduced in the bandgap as the results of polaron and bipolaron formation. Solid and dash-line arrows represent electron spin and possible transition to/or from the new states, respectively. The charge and spin of the polarons are listed to the right.
2.6  *Solubility of the conjugated polymer*

Another important property of conjugated polymers is that they can be made soluble in common organic solvents by adding appropriate functional side-chain groups. This means that the deposition of polymer films can be done by spin-coating techniques in air from polymer solutions, which makes fabrication of conjugated-polymer-based thin-film devices much easier and less costly when compared with devices made *via* vacuum deposition techniques. The interaction at the interface between a polymer in an organic solvent and the substrate surface affects the formation and morphology of the film. This may influence the mechanism of exciton and charge carrier transport, dissociation of excitons and recombination of charges in various electronic devices, and therefore influence the performance of the resulting devices\textsuperscript{21}. It again shows that characterization and modification of surfaces are essential in improving the performance of opto-electronic devices.
3. **Surface energy modification**

3.1 **Surface energy**

When a liquid drop stands on a solid surface, the shape of the droplet is determined by a balance between the cohesive force existing between the liquid molecules and the attractive force formed between the liquid molecules and the solid surface molecules at the interface. A droplet beads-up when the cohesive force is stronger than the attractive (adhesion) force. On the other hand, the liquid drop spreads over a solid surface if the cohesive force is weaker than the attractive (adhesion) force. The angle formed between the liquid-solid interface and a tangent to the droplet profile at the liquid-solid-air contact point is referred to as the contact angle ($\theta$), which is often used to qualitatively represent surface energy or surface wettability. In Fig. 3.1, a schematic diagram of a droplet standing on a solid surface at equilibrium is shown, where $\sigma_{SL}$, $\sigma_S$, and $\sigma_L$ are the surface energies at the interfaces of the solid-liquid, solid-air and liquid-air, respectively. $\theta$ is the contact angle.

![Fig. 3.1. Schematic diagram of a liquid droplet standing on a solid surface.](image)

At equilibrium, the relationship between the shape of a liquid droplet and the surface energy or surface tension at the interfaces can be quantitatively stated by Young’s equation:
\[
\sigma_L \cdot \cos \theta = \sigma_S - \sigma_{SL}
\]
\[
\Rightarrow \cos \theta = \frac{\sigma_S - \sigma_{SL}}{\sigma_L}
\]

Eqn 3.1

The surface energy or the surface wettability of a solid surface can be characterized using the contact angle. The relationship between the contact angle and the surface wettability is illustrated in table 3.1.

**Table 3.1.** The contact angle of water on a solid surface and its surface wettability

<table>
<thead>
<tr>
<th>Forces</th>
<th>Contact angle</th>
<th>Surface wetting capability</th>
<th>Surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion force &gt;&gt; Cohesive force</td>
<td>( \theta \sim 0^\circ )</td>
<td>Completely wettable</td>
<td>Higher</td>
</tr>
<tr>
<td>Adhesion force ( \geq ) Cohesive force</td>
<td>( 0^\circ &lt; \theta \leq 90^\circ )</td>
<td>Partially wettable</td>
<td></td>
</tr>
<tr>
<td>Adhesion force &lt; Cohesive force</td>
<td>( \theta &gt; 90^\circ )</td>
<td>Non-wettable</td>
<td>Lower</td>
</tr>
</tbody>
</table>

In practice, a contact angle when a liquid covers a fresh solid surface (i.e. the advancing contact angle) differs from that when the liquid recedes (i.e. the receding contact angle). Values quoted in the literature generally refer to the advancing contact angle, unless otherwise stated.

3.2 Determination of contact angle with goniometry, Wilhelmy balance and capillary rise methods

To characterize the surface energy or surface wettability, several methods have been developed, including (a) measuring the contact angle of a pendant droplet on a surface using goniometry (drop shape method)\(^{22-24}\) and (b) calculating the contact angle that is formed between a solid surface and a liquid when a solid plate is vertically immersed into a liquid, using a Wilhelmy
balance (Wilhelmy method)\textsuperscript{25,26}. These are schematically illustrated in Fig. 3.2. Additionally, capillary rise\textsuperscript{27-29} can be also used to characterize surface energy.

3.2.1 Determination of the contact angle by a goniometer

Goniometry, measuring the contact angle of a pendant liquid droplet on a surface, is a convenient and direct method. As shown in Fig. 3.2 (a), a pendant liquid droplet is dispensed on a surface using a micro syringe attachment. The contact angle is measured using a goniometer at room temperature and ambient humidity immediately after equilibrium is established.

![Schematic diagrams of contact angle measurement instruments: (a) Goniometry and (b) Wilhelmy balance. The substrate in (b) consists of a coated layer and a supporting substrate layer. In the general case $\theta \neq \theta_m$.](image)

The contact angles of some of the conjugated polymers, including polythiophenes, polyfluorene copolymers and a fullerene derivative used to fabricate the polymer solar cells and light emitting diodes in our lab, were measured using the drop shape method. The samples were prepared by spin-coating a polymer film onto a glass substrate from a polymer solution under ambient conditions. Water was used as the probe liquid for the measurement and all measurements were made under ambient conditions. The chemical
structures, film formation, storage conditions and contact angle values are listed in Table 3.2. The polymers from (1) to (11) belong to the polythiophene family. These polymers can be divided into roughly two groups from a chemical structure point of view. The first group of polymers, including (1) to (5) and (10) to (11), has side chains with alkyl, or phenyl alkyl groups attached to the backbone. These hydrophobic side chains cause the films to be non-wettable and therefore show higher contact angles (θ > 90˚) as compared with the other polythiophenes. The second group of polymers consists of (6)-(8), which have ether groups as side chains with an alkyl terminating group, and might result in attractive (adhesion) forces (O-HO bond) between the polymer surface and the water (the testing liquid), resulting in films that are more wettable (θ < 90˚). Polymer (9) is also a polythiophene and involves both alkyl and ether groups in its side chains. The contact angle for this polymer is larger than 90˚, possibly because of the hydrophobic alkyl groups dominating the surface energy property of the outer layer of the film. Polymers (12) and (17) to (20) are alternating polyfluorene copolymers and non-wettable, as governed by the alkyl group. A film from the C₆₀ molecule derivative has a contact angle less than 90˚, which could be attributed to the ester group involved in the molecule. The difference in contact angle between polymers (for example polyfluorene copolymers) and the PCBM fullerene might cause an inhomogeneous distribution of two phases laterally, and/or a gradient distribution vertically relative to the surface as spin-coated from a mixture solution, as revealed by other analysis methods\textsuperscript{30,31}.

The condition for preparing films (spinning speed, spinning duration and solution concentration), in our case, did not have much influence on the resulting contact angle as shown in Table 3.2.

3.2.2 Determination of the contact angle using a Wilhelmy Balance

As shown in Figure 3.2 (b), a thin plate (generally rectangular) coated with a thin film layer is immersed into and withdrawn from a liquid at a constant
<table>
<thead>
<tr>
<th>Short name</th>
<th>Chemical structure</th>
<th>Spin rate</th>
<th>Duration (s)</th>
<th>Drying in</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) PTOPT</td>
<td><img src="image1" alt="Chemical structure" /></td>
<td>1000</td>
<td>40</td>
<td>X</td>
<td>98</td>
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<td></td>
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<td></td>
<td></td>
<td>90</td>
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<tr>
<td>(2) PDOPT</td>
<td><img src="image2" alt="Chemical structure" /></td>
<td>1000</td>
<td>40</td>
<td>X</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>109</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>20</td>
<td>X</td>
<td>107</td>
</tr>
<tr>
<td>(3) POPT</td>
<td><img src="image3" alt="Chemical structure" /></td>
<td>1000</td>
<td>40</td>
<td>X</td>
<td>101</td>
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<td></td>
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<td></td>
<td>90</td>
</tr>
<tr>
<td>(4) P3HT</td>
<td><img src="image4" alt="Chemical structure" /></td>
<td>1000</td>
<td>40</td>
<td>X</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>94</td>
</tr>
<tr>
<td>(5) P3OT</td>
<td><img src="image5" alt="Chemical structure" /></td>
<td>1000</td>
<td>40</td>
<td>X</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>(6) PEOPT</td>
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<td></td>
<td>78</td>
</tr>
</tbody>
</table>

- All films were deposited from chloroform solution with concentration of 5 mg/ml. Unless otherwise stated.
- Vac$^a$: In a vacuum, $10^{-6}$ Torr; Air$^b$: In air; Adv$^c$: advancing contact angle; and Rec$^d$: receding contact angle.
speed so that a curved liquid surface is formed on both the back and front sides of the plate. The force, \( F \), acting on the plate is monitored by a micro-electro balance and can be described by the following equation:

\[
F_{\text{total}} = \text{wetting force} + \text{weight of plate (sample)} - \text{buoyancy}
\]

For a “Sigma 70” Wilhelmy balance, as used in this work, the weight of the plate is removed by the instrument’s electronics and the buoyancy force is estimated by extrapolating a graph of force vs immersion depth back to zero depth. The remaining component of the measured force is the wetting force which is given by:

\[
\text{Wetting force} = \gamma_{LS} \frac{P \cos \theta + \cos \theta_m}{2}
\]

\hspace{1in}\text{Eqn. 3.2}

where \( P \) is the perimeter of the sample plate, and \( \gamma_{LS} \) is the interfacial surface tension between the liquid and solid surfaces. \( \theta \) and \( \theta_m \) are the contact angles of the liquid formed on the film-coated side and backside of the plate, respectively. They are normally not equal due to the unequal surface energy of the two sides. Thus, at any depth, data is collected which can be used to calculate the contact angle. The contact angle that is obtained from data generated as the sample plate advances into the liquid, is called the ‘advancing contact angle’. When the process is reversed, \( i.e. \) as the sample plate retreats from the liquid, a ‘receding contact angle’ is obtained. Here it is assumed that the surface tension of the liquid and the contact angle of the liquid on the backside of the substrate, \( \theta_m \), are known. The dynamic contact angle measurement can be carried out while the plate is immersed into the liquid. In paper\(32\), we demonstrated the \textit{in-situ} surface energy (contact angle) investigation of conjugated polymers during electrochemical doping in an aqueous electrolyte using the Wilhelmy method.

3.2.3 Determination of the contact angle by capillary rise

The capillary rise, \( H \), due to the capillary interaction of a surface and a liquid can be used to evaluate the surface energy of a solid surface. \( H \) can be estimated from the following equations for different geometries\(28,29,33\).

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Cylinder tube:  \[ H = \frac{2\gamma_{lv} \cos \theta}{\Delta \rho g R} \] \quad Eqn. 3.3

Plate:  \[ \sin \theta = 1 - \frac{\Delta \rho g H^2}{2 \gamma_{lv}} \Rightarrow H = \sqrt{\frac{2\gamma_{lv} (1 - \sin \theta)}{\Delta \rho g}} \] \quad Eqn. 3.4

where \( \Delta \rho \) is the difference between the densities of the liquid and vapour, \( \gamma_{lv} \) is the surface tension of the liquid, \( g \) is the acceleration due to gravity and \( R \) is the radius of the cylinder tube.

In our contact angle determination, we qualitatively demonstrated the surface energy changes through the capillary rise on the inner and outer surfaces of a sample consisting of two parallel polymer coated plates when subjected to electrochemical doping at different doping levels.

![Fig. 3.3. A front view of a sample that consisted of two P3HT coated ITO/PET parallel plates facing each other, when subjected to electrochemical doping at different doping levels.](image)

The capillary rise of an aqueous electrolyte between two parallel plates coated with P3HT was quite obvious when the samples were subjected to electrochemical doping.

The meniscus shape in Fig. 3.3 was mainly attributed to the difference between the capillary fall \((H_2)\) on the inner surface, the capillary rise \((H_1)\) on the outer surface of the two parallel plates and to an external term \(H(d, L)\) induced by sample geometry. The total capillary rise difference, \( \Delta H_{\text{total}} \), is given by

\[ \Delta H_{\text{total}} = H_1 - H_2 + H(d, L) = \sqrt{\frac{2\gamma_{lv} (1 - \sin \theta_1)}{\Delta \rho g}} + \sqrt{\frac{2\gamma_{lv} (1 - \sin \theta_2)}{\Delta \rho g}} + H(d, L) \] \quad Eqn. 3.5
where $\theta_1 \approx 76^\circ$ and $\theta_2 \approx 110^\circ$ are the contact angles of the liquid against the outer and inner sides of the sample, respectively, at initial state. $d$ and $L$ are the distance between two parallel samples and the width of the samples, respectively. As shown in Fig. 3.3, $\Delta H_{\text{total}}$ decreases with increasing doping level, revealing a reduced capillary fall on the inner side of the sample, resulting from a decreased contact angle, $\theta_2$. $\theta_1$ did not change, and the capillary rise $H_1$ was kept unchanged. $H(d , L)$ only underwent a minor change which was considered negligible, because there was no geometry change. The trend in wettability changes of P3HT film is consistent with the results obtained from the Wilhelmy balance and the drop shape measurements\textsuperscript{32}.

The surface energy or wettability of a solid surface can be characterized by the contact angle. Three methods including goniometry, Wilhelmy balance and capillary rise were presented. Goniometry is simple and direct. It only supplies information at a local point (on the focusing plane of the meridian) for each measurement. Surface heterogeneity and/or roughness could cause variations of the contact angle along the three-phase line. Drop size differences can be a further cause of variation of the contact angle in the measurement\textsuperscript{34-36}. The contact angle measurement is accomplished with a sensitive microbalance and hence is free from operator error which would arise if it were determined by eye. The results also tend to be highly reproducible due to the large scan area of the samples and the bulk liquid.

On the other hand, the Wilhelmy balance method has the advantage of giving reliable characterization of the dynamic effect during wetting and dewetting because of accurate control of the advancing and receding speeds. The capillary rise on a vertical plate can also give an \textit{in-situ} contact angle characterization. It requires precise height monitoring of the sample.

To make the capillary effect more effective, strategies for preparing a sample should be considered and curvatures formed at the interface between the three phases (gas, solid and liquid) must be precisely identified and taken into account in the calculation.
Surface wettability is determined by the surface molecules and their orientation. Additionally, properties of roughness, inhomogeneities and chemical contamination have been shown to have smaller effects on surface wettability.

3.3 Surface energy modification

In current materials research and development, a high priority is given to surface modification techniques to achieve improvements of surface properties for specific applications requiring high quality, thin films (e.g. for thin film opto-electronics, for patterning of material on a surface as well as for painting \(^{37-39}\)). Surface energy modification works best when restricted to a very thin layer at the surface, just a few nm or even smaller. Ideally the modified layer should be a monolayer of a polymer surface, such that the surface property, for instance surface wettability, is modified and the bulk properties beneath the surface are kept unchanged. The common method to modify a surface property will be discussed in this section. The method using a bare rubber stamp will be demonstrated in section 3.4.

3.3.1 Mechanical surface modification

Atomic Force Microscope (AFM) was initially developed to image the surfaces of insulating materials. However, it was discovered that an AFM probe could cause mechanical modifications to a surface\(^{40,41}\). Mechanical surface modification can be regarded as the simplest method to modify a surface: just using a probe of an atomic force microscope scratches a surface with a controlled force in either contact or semi contact mode. A very thin layer is removed and the surface morphology is altered. The modified surfaces are dependent on the shape of the tip, the force strength applied to the tip, the scanning speed of the tip and the morphology of the surface as well as the hardness of the surface material. In some cases tip-induced reorganisation of molecules or chemical reaction of the surface molecules may occur\(^{42,43}\).
3.3.2 Plasma treatment of surface

Plasma is an ionised medium consisting of electrons, ions and possibly of neutral species and photons, which meets some additional criteria\textsuperscript{44}. Plasma treatment is probably the most versatile surface treatment technique. Plasma surface treatment can be conducted using several gases: oxygen, nitrogen or carbon dioxide, depending on the surface’s composition\textsuperscript{45}. Oxygen plasma treatment resulted from cross-linking of the surface atom with an ionised oxygen atom can increase surface energy or surface hydrophilicity or surface wettability, because some of the oxygen sites are readily converted into hydroxyl bonds and easily attract water molecules. The chemical structure of a shallow surface layer (a few nm) can be changed significantly, while the bulk properties remain unchanged. A similar process takes place with N\textsubscript{2} plasma treatment. Schematic illustrations of both treatments of a surface are shown in Fig. 3.4.

![Chemical structures of plasma treatment](image)

**Fig. 3.4.** A schematic illustration of O\textsubscript{2} and N\textsubscript{2} plasma treatment of a surface.

The change of surface energy or surface wettibility after plasma treatment basically depends on the gas selected, active gas pressure, the voltage applied
to the plasma, the temperature of the plasma gas and the time that the plasma is in contact with the surface.

3.3.3 Self-assembled monolayer (SAM)

A self-assembled monolayer (SAM) is formed spontaneously by chemisorption and self-organization of functionalised and long-chain organic molecules on surfaces of an appropriate substrate. SAMs are usually prepared by immersing a substrate into a prepared solution containing a ligand that is reactive with a surface or by exposing the substrate to a vapor or a reactive species for a period of time. Self-assembled monolayers of thiols on gold surfaces are widely used to produce model surfaces with well-defined chemical composition for a variety of applications including electronic devices, biomaterials and biosensor surfaces\textsuperscript{4,6,41,46}. A SAM layer may also be transferred to a surface by contact printing using a rubber stamp\textsuperscript{47}. The SAM layer is sometimes called the ‘ink’. The surface energy or surface wetting capability can be tailored by selecting the terminating functional group of the SAM molecule appropriately, by adjusting the length of the moiety and by adjusting the degree of coverage of the moiety on the surface. A SAM layer also has the function of blocking any reaction between two interfaces when situated between them\textsuperscript{48}. It has been demonstrated that some techniques, such as micro contact printing (µCP) using PDMS\textsuperscript{49,50}, photolithography\textsuperscript{51} and vapor deposition can be used to modify a surface and even produce chemically patterned surfaces.

Further to the above-mentioned methods, thermal annealing is also an efficient and common way to reorder the orientation of molecules in a film as well as to modify surface morphology. Photochemistry using UV or ozone can also be used for surface modification, as well as ion implantation and electrochemical doping\textsuperscript{52,53}.

3.4 Surface modification by bare PDMS stamp

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Transferring a poly(dimethylsiloxane) (PDMS) molecule to a surface when a PDMS stamp is brought into conformal contact with the surface has been reported by Glasmästar\textsuperscript{54}. In this section a method of surface energy modification using a bare PDMS stamp is presented. The mechanism for surface energy modification was investigated by several surface analysis methods including atomic force microscopy (AFM), infrared absorption spectroscopy (IRAS) and contact angle measurement.

The possibility of using a bare PDMS stamp to modify the surface energy of a surface was first observed to generate a thin layer pattern on a surface. Finally the method is developed and used as an efficient and common tool for modifying surface energy and for patterning polymers\textsuperscript{55-57} and biomolecules\textsuperscript{58,59}. The surface energy modification is performed as illustrated and described in Fig. 3.5.

**Step 1:** Prepare a solid surface.

**Step 2:** A flat or patterned PDMS stamp makes conformal contact with the prepared surface for a period of time.

**Step 3:** Removal of the stamp from the surface leaves a PDMS modified surface.

**Fig. 3.5.** A schematic illustration for surface modification by a bare PDMS stamp.

Surface energy changes with time were monitored when a stamp was brought into conformal contact with a surface. Fig. 3.6 shows the contact angle of two surfaces, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) and the polyelectrolyte poly(sodium-4-styrenesulfonate) (NaPSS), as a function of contacting time. Contacting time is defined as the period from when the sample is brought into contact with the surface until when the stamp is removed. N-hexadecane was used as the probe liquid. It can
be seen that the natural contact angle of PEDOT-PSS ($\theta_1$) is ~ 36° and ~ 9° for NaPSS ($\theta_2$); thus the wetting by n-hexadecane on PEDOT-PSS is poorer than that on NaPSS. The contact angle on PEDOT-PSS or NaPSS changes with contacting time. The contact angle of the n-hexadecane on PEDOT-PSS decreases from 22° to 12° logarithmically as the contacting time changes from 25 min. to 100 hrs. For NaPSS, the contact angle increased linearly from 27° to 33° with logarithmic contacting time from 25 min. to 100 hrs. The difference in contact angle between modified and unmodified films is -25° for the PEDOT-PSS film. The magnitude of the corresponding angle for the NaPSS was less, +23° (contacting time: 2 days or more), revealing that the surface energy modification was undertaken and done mostly during the first four hours.

![Graph](image)

**Fig. 3.6.** The contact angles as a function of contacting time when PEDOT-PSS and NaPSS surfaces were getting conformal contact by bare stamps.

The surface morphology of the areas that were modified or non-modified was investigated using atomic force microscopy (AFM)\textsuperscript{55} revealing that a larger thickness (a few nanometers) protruded from the modified surface relative to the non-modified surface. However it was difficult to judge if the height change was caused by the lifting up of the original film from the surface.
or due to molecule transfer from the stamp to the surface or possibly due to an absorbed layer of water, since the measurement was carried out in the air.

The infrared absorption spectroscopy (IRAS) in Fig. 3.7 gives an insight into the mechanism of the surface energy modification method. The IRAS investigation, firstly, shows the chemical changes on PEDOT-PSS and NaPSS surfaces due to the modification. They are similar with only minor differences, suggesting that the chemical changes are the same on both surfaces. The chemical changes are related to the uncured PDMS molecules, implying small PDMS molecules have been transferred to the surface during the conformal contacting of the PDMS stamp with the surfaces.

**Fig. 3.7.** IRAS of PEDOT-PSS and NaPSS films before and after modification by a PDMS stamp. Left: IRAS spectra of a PEDOT-PSS film on gold before (a) and after (b) PDMS modification and the resulting difference (b)-(a) spectra (e). The IRAS spectra of a NaPSS film on gold before (c) and after (d) and the resulting difference (d)-(c) spectra (f). Right: The resulting spectra of residual PDMS on PEDOT-PSS and NaPSS are compared with the spectra of oligo-DMS and PDMS. The spectra of PDMS and ODMS are scaled for easier comparison.
3.5 Surface modification by electrochemical doping

As already shown in sections 3.2.2 and 3.2.3, modification of the surface energy of a conjugated polymer film can also be carried out when subjected to electrochemical doping in an electrolyte. Polymer surface energy changes can be attributed to the fact of change in polarisability due to the semiconductor/metal transition occurring and change of surface chemical composition due to ingress/egress of anions/cations and associated solvent molecules during the electrochemical doping. Fig. 3.8 shows the dynamic surface energy changes of two polythiophene films during electrochemical doping-dedoping, measured in-situ by the Wilhelmy Balance method.

![Fig. 3.8. In-situ dynamic contact angle of (a) poly(3-hexylthiophene) and vapor-phase polymerised poly(3,4-ethylenedioxythiophene) upon electrochemical doping-dedoping.](image-url)

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4. **Patterning of polymers on a PDMS modified surface**

4.1 **Patterning of polymers using soft lithography**

Soft lithography has been developed in recent years to generate micro or nano-patterns for application in biology, biochemistry and electronics\(^7,49,50,62\). Due to its simplicity, low cost, no clean room requirement and the possibility for patterning on a curved surface and over a large area, soft lithography is an attractive alternative to photolithography. The big advantage of soft lithography is that it avoids exposing a polymer to high energy irradiation and therefore protects a polymer from degradation. The essential tool used in soft lithographic techniques is a transparent elastomeric (rubber) poly(dimethylsiloxane) (PDMS) stamp. By using a stamp with the desired micro or nano-topography patterns, fluids carrying dissolved polymers or dispersed particles can be directly confined, solidified and patterned onto a surface by means of methods like micromolding in capillaries (MIMIC)\(^63\), microtransfer molding (\(\mu\)TM)\(^64\) and micro contact printing (\(\mu\)CP)\(^49,50\). A polymer layer is softened by heating at certain temperature or solvent vapor and can be soft embossed (EM) or imprinted\(^7\).

A development of soft lithography is patterning of a polymer onto a chemically patterned or modified surface that is created by transferring a molecular monolayer pattern using the SAM method or stamping ‘ink’\(^49\). Dewetting of the polymer on some area of the chemically heterogeneous surface replicates the surface pattern. Intensive experimental studies and theoretical simulations of this issue have been performed since the end of the 20th century\(^65-76\).

The instability of films, as caused by variation of film thickness\(^67,68,76\) and surface energy gradient on a surface, causes dewetting and hence plays an important role in initiating patterning processes\(^74,77-80\). Film instability that
induces dewetting or rupture of a thin film can be classified into two regimes: film instability on a homogeneous substrate and that on a heterogeneous substrate. A classical model of thin film break up on a homogeneous substrate is called spinodal dewetting. The inflection points, given by the second derivative of changes of Gibbs free energy is equal to zero, are called spinodal points, which define the thermodynamic limits of metastability. For heterogeneous substrates, the break-up is described by the capillary instability mechanism. Surface energy is the driving force for the film rupture process.

Instability of thin films on a heterogeneous surface results from a spatial difference in the wettability of the surface or the gradient of surface energy and not from the surface being completely nonwettable.

A thin-film equation has been used to describe film instability and rupture, and to predict ideal templating, which must be reviewed in order to get a desired polymer pattern. The nondimensional thin film equation:

\[
\frac{\partial H}{\partial T} + \nabla \cdot \left[H^3 \nabla (\nabla^2 H)\right] - \nabla \cdot \left[H^3 \nabla \Phi\right] = 0. \tag{Eqn. 4.1}
\]

has been used to simulate instability of liquid films on heterogeneous substrates and to predict the conditions for an ideally templating substrate surface. The nondimensional equation governs the stability and spatio-temporal evolution of a thin film system on a substrate subjected to excess intermolecular interactions. The terms in Eqn. 4.1 are as follows: \(H(X,Y,T)\) is the nondimensional local film thickness scaled by the mean thickness \(h_0\); \(\Phi = \frac{2\pi h_0^3}{|A_s|} \times [\frac{\partial \Delta G}{\partial H}]\), \(\Delta G\) is the excess intermolecular interaction energy per unit area, and \(A_s\) is the effective Hamaker constant for van der Waals interaction; \(X, Y\) are the nondimensional coordinates in the plane of the substrate, scaled by a length scale \((2\pi \gamma / |A_s|)^{1/2} h_0^2\); and the nondimensional time \(T\) is scaled by \(12 \pi^2 \mu \gamma h_0^5 / A_s^2\), \(\gamma\) and \(\mu\) refer to the film surface tension and
viscosity, respectively. The terms (from left to right) in the thin film equation correspond to the accumulation, curvature (surface tension) and intermolecular force.

The length scale of the spinodal instability on a uniform surface is given by 
\[ \left( \frac{4\pi^2 \gamma}{\partial^2 \Delta G / \partial h^2} \right)^{1/2}. \]

On a chemically heterogeneous, striped surface:
\[ \Phi = \Phi(H, X, Y). \]

At a constant film thickness, variation of \( \Phi \) in the \( X \) direction by a periodic step function of periodicity \( L_p \), the gradient of force, \( v \Phi \), at the boundary of the stripes causes flow from the less wettable (high pressure) regions to the more wettable (low pressure) regions, even when the spinodal stability condition \( \partial \Phi / \partial H > 0 \) is satisfied everywhere. The nonlinear thin film equation predicts that there is a critical length scale \( (\lambda_h) \) that is smaller than the length scale of the spinodal instability. Ideal replication of substrate surface energy patterns in thin film morphology occurs only when

(a) the periodicity of the substrate pattern is greater than \( \lambda_h \);
(b) the width of the less wettable stripe is within a range bounded by a low critical length, below which no heterogeneous rupture occurs, and an upper transition length above which complex morphological features bearing little resemblance to the substrate pattern are formed;
(c) the contact line eventually rests close to the stripe boundary;
(d) the liquid that forms on the more wettable stripe remains stable.

Conditions (a) and (b) ensure the onset of dewetting at the center of every less wettable site and conditions (c) and (d) ensure full coverage of every more wettable site.

In summary, the conditions for ideal replication of a periodic heterogeneous substrate can be engineered by modulating the pattern periodicity, the width ratio between less and more wettable strips, the film thickness and the wettability gradient across the boundary.
4.2 Patterning of polymers on PDMS patterned surface by dewetting

As demonstrated in section 3.4, a PDMS stamp is capable of modifying the surface energy of a surface by simple conformal contacting with the surface. We developed microcontact printing to create a chemically patterned surface. The method to pattern a surface is simple and convenient compared with the SAM method, since only a bare PDMS stamp without any coating is used. A PDMS stamp leaves a low molecular weight residue, as an ‘ink’ on a surface, as observed by infrared spectroscopy after removal of the stamp\textsuperscript{54,55}. Patterning of single or double layer conjugated polymers can be achieved by dewetting according to the substrate’s or lower layer’s surface energy pattern, as applicable, from a solution with a low vapor pressure or from a film that is heated and subsequently melted. Several issues have been addressed in this thesis work, including solvent effects on the patterning method\textsuperscript{55,56,82}; the profile of patterns prepared from different methods\textsuperscript{55,56,82}; the thickness dependence of pattern morphology from melts\textsuperscript{56,82} and the aspect ratio of the spherical caps of patterned films formed from melts\textsuperscript{56}. A schematic picture in Fig. 4.1 summarizes the surface energy controlled dewetting technique. The details are also briefly discussed in the following sections.

a. How a solvent effects patterning methods:

On a PDMS patterned surface (see the 1\textsuperscript{st} column in Fig. 4.1) there are two different methods for patterning of the polymers, depending on the solvent used for dissolving the polymer (see the 2\textsuperscript{nd} to 4\textsuperscript{th} columns in Fig. 4.1). A polymer dissolved in solvents (toluene, xylene and (di)chlorobenzene) with low vapour pressure (< 0.03 bar) and low evaporation rate can be patterned directly from the solution by spin-coating or dip coating (the 2\textsuperscript{nd} column in Fig. 4.1). However, a polymer dissolved in a solvent (chloroform and hexane) with high vapor pressure (> 0.2 bar) and fast evaporation rate forms a continuous film on
top of the modified surface when spin-coating. The patterning of a polymer can be obtained when the polymer film is annealed above its glass transition point (The 3rd and 4th columns in Fig. 4.1).

**Surface patterning**

**Patterning polymer with 2 different methods**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Applying PDMS stamp</th>
<th>Removal of stamp leaves pattern</th>
<th>Layer 1 Transfer from solution directly</th>
<th>Layer 1 Transfer upon annealing</th>
<th>Layer 2 Transfer upon annealing</th>
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<td>Substrate coated with the homogeneous polymer 1</td>
<td>Annealing at $T &gt; T_{m1}$</td>
<td>Layer 1 coated with the homogeneous polymer 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Formation of layer 1</td>
<td></td>
<td>Formation of layer 2 on top of layer 1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta \theta_1 = 24^\circ$</td>
<td>$\Delta \theta_2 = 33^\circ$</td>
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</tbody>
</table>

**Fig. 4.1.** The illustration of surface modification as well as two different patterning methods on a modified surface. Method 1: Formation of a polymer pattern directly from a solution by spin-coating. Method 2: Formation of single and double layer polymer pattern from a homogeneous film upon annealing.

**b. Profile of patterned polymer with different methods:**

In “method 1”, films patterned directly from a solution by spin-coating (Fig. 4.2a) typically have a U-shaped profile consisting of two high walls at the pattern’s edge and a flat interior part between the two walls. The ratio between the height of the wall and the thickness of the interior part is in the range from ~1 to 7, depending on the deposition conditions (spinning speed, solution
concentration and selected solvent). The patterned film thickness (flat interior part) was limited to 200 nm. This profile results from liquid film dewetting, solvent evaporation and mass transfer. The polymer carried by a solvent first dewets from a less wettable region and collects onto the more wettable region. The solute is then deposited (pinned) at the solid-liquid contact line. Mass transport to the edge is undertaken during solvent evaporation, leading to a thicker film at the edges. At higher concentration, the height of the U-shapes is reduced (Fig. 4.2b) due to a short time for mass transfer to the edge\textsuperscript{83,84}. On the other hand, when homogeneous polymer films form on the PDMS stamp patterned surface, pattern formation of the polymer can be induced by annealing at a temperature above $T_g$. This is “method 2” for replicating a surface pattern. The polymer film patterns upon annealing at the final stage of method 2 always have a spherical-cap shape (Fig. 4.2c) due to minimization of the surface energy.

![Fig. 4.2. The cross sections of a patterned polymer](image)

(a) polyfluorene from a 10-mg/ml solution by spin-coating (1500 rpm), (b) polyfluorene from a 20-mg/ml solution by spin coating (1000 rpm) and (c) from a polythiophene 300 nm thick film upon annealing.
c. Influence of film thickness on morphology

The dewetting of a polymer film upon annealing shows that the time period for patterning varies from a few minutes to several hours. The length of time required is determined by the parameters of heating rate, temperature, polymer thickness, molecular weight of the polymer, and surface energy gradient across the boundary of the less and more wettable regions. Not all films can generate desirable, perfect patterns. Only those films with initial film thicknesses in an intermediate range can perfectly replicate surface pattern. A thinner film is more likely to form holes and then to break into several small holes and further form smaller defect droplets (called dewetting spots) in less wettable regions. At low initial thickness, the density of dewetting spots is larger than that found with larger thickness, and the size of dewetting spots is smaller than those formed with larger thickness. At intermediate thickness, perfect patterns with clean and smooth array on the modified substrate surface can be obtained. The film is hard to move and remains stable when the initial film thickness is too large.

Fig. 4.3 shows an example of film morphology dependence on thickness from measurements taken by AFM in tapping mode. The modified surface had a periodicity of 7.5 µm, consisting of more wettable stripes 3.5 µm wide and less wettable ones 4.0 µm wide.
Fig. 4.3. Comparison of PMMA film morphologies with varied initial film thickness (a) 120 nm, (b) 128 nm, (c) 345 nm, (d) 500 nm.

Similar trends in morphology are observed for all studied periodicities, from 1-100 µm.

The graph in Fig. 4.4 shows the relationship of pattern morphologies with pattern periodicity and initial film thickness. It can be divided into three regions, denoted by I, II, and III. Regions I and III are the undesired regions where clear and smooth patterns could not be achieved due to either too thick or too thin films. Region II is the intermediate range of thickness, relative to the periodicity, that is suitable for creating perfect patterns. This intermediate range of film thicknesses broadens with an increase of the pattern dimension. To get desired pattern arrays, for PMMA, for instance, a thicker film (> 200 nm) is necessary for patterning of a large structure (periodicity larger than 10 µm) and a thin film (< 50 nm) for a tiny structure (periodicity less than 1 µm). The thickness of the film influences the morphology of the patterned film more strongly than other parameters, such as the stamping time and the heating rate for the melting of the film.
Fig. 4.4. A plot of the thickness ranges of a film versus the periodicity of a film pattern. ◯ and □ are the higher and lower thickness limits, respectively, between which perfect patterns may be obtained.

d. Aspect ratio of the spherical cap of a patterned film upon annealing:

During the final stage of annealing, the patterned film has a cross section of spherical cap shape as shown in Fig. 4.4. To explore the maximum height of the spherical cap, the patterned polymer structures were measured using AFM. The patterned polymer structure presented a smooth, clear cylindrical cap. The polymer structures were physically separated. A plot of the maximum aspect ratio versus the width of the obtained spherical cap is presented in Fig. 4.5. It shows that the ratio is limited to 0.15 and occurs for
structures with 10 µm periodicity. This reflects the interactions between the materials of the modified substrate surface and the overlying polymer film.

**e. Imaging of patterned polymers:**

Fluorescent polymers such as polythiophenes, CDT-green and CDT-red, can be dissolved in low vapor pressure (low evaporation rate) organic solvents, and therefore can be patterned on to a PDMS modified PEDOT-PSS surface directly from solution (Fig. 4.6).

![Fig. 4.6. Photographs of patterned polythiophene (a), CDT-green (b) and CDT-red (c) polymer with different geometry spin-coated from dichlorobenzene solution (10 mg/ml of and 1000 rpm), xylene (10 mg/ml and 100 rpm), respectively. The colored areas are patterned polymers under light excitations. The dark areas are exposed substrate surface (PEDOT-PSS).](image)

When a polymer has a desirable glass transition point, such as polythiophene (PDOPT \( T_g = 90^\circ C \)) and poly(methyl methacrylate) (PMMA \( T_g =106^\circ C \)) and can be dissolved in a high vapor pressure (high evaporation rate) solvent, patterning single or bilayer polymer can be achieved from an initially flat film upon annealing (see Fig. 4.7, Fig. 4.8 and Ref.\(^{56}\) for details).
Fig. 4.7. AFM height image of structures formed upon annealing from continuous films. (a) Patterned PDOPT film with periodicity of 1.66 µm and (b) patterned PMMA film with a periodicity of 450 nm and (c) submicron diameter ordered spherical dots of PMMA. The initial film thicknesses are 120 nm, 20 nm and 80 nm for (a), (b) and (c), respectively.
In summary, patterning of a polymer from a solution or its melt by surface energy controlled dewetting on a bare PDMS modified surface has been demonstrated. Physical properties of the solvent are key factors that affect the methods for the patterning process. The profile of a patterned polymer directly from a polymer solution can be controlled by the deposition conditions. If a continuous polymer film is formed, patterning of the polymer can be achieved by dewetting upon annealing. The morphology of patterned films is strongly
influenced by the initial film thickness. A desirable film pattern can be formed at an intermediate range of the film thickness. The range enlarges with an increase of pattern periodicity. The cross section of a pattern after the final annealing stage has a spherical shape and is affected mainly by the interactions between the polymer melts and the solid surface.

The surface energy controlled patterning technique supplies a convenient and quick way for creating a modified surface and generating smooth, completely physically separated polymer structures. The method that can generate a conjugated polymer pattern on a conducting polymer surface is unique. It is very promising in generating double and multilayer polymer arrays [see Fig. 4.8 and Ref.56] and consequently fabricating conjugated polymer-based opto-electronics. Properties such as photonic bandgap structure on a surface, polarized or white light emitting diodes prepared with the method might be achieved85.
5. **Conjugated polymer-based optoelectronics**

The conjugated polymer-based optoelectronics dealt with in this thesis include polymer light emitting diodes (PLEDs) prepared from polymers doped with phosphorescent metal compounds and polymer/fullerene bulk heterojunction solar cells (PSCs). The conjugated polymers are the main component of an active layer (~ 100 nm thick), sandwiched between two electrodes. PLEDs generate light, namely electroluminescence, by injection of charges into the polymer layer, where recombination of the charges takes place (see Fig. 5.1). PSCs create an electric current via the process of absorbing light into a polymer, and through the following steps: exciton dissociation, charge transport and collection (see Fig. 5.4). PLEDs and PSCs are devices which convert energy in opposite directions: PLEDs take electricity and convert it to light, while PSCs do the reverse.

5.1 *Polymer light emitting diodes (PLEDs)*

The first PLED was reported in 1990\(^1\). It attracted considerable interest due to the advantages of low operating voltage, easy fabrication and wide-view angle. The advantage of thin and flexible PLEDs is that they are made completely from polymers. The main applications of PLEDs are as indicators, displays and lightning sources where enhancement of the light output power efficiency is of importance.
Fig. 5.1. Schematic diagram of working mechanism of a single-layer PLED. Procedure ①: Injection of charges to the active polymer layer from two electrodes; Procedure ②: charge transport in the polymer layer; Procedure ③ recombination of charge gives off light.

Fig. 5.1 shows the schematic working principle of a single-layer PLED. Three steps are involved: injection of charges into the active polymer layer from two electrodes; charge transport in the polymer layer and formation of an exciton or excited state; and then recombination of the charges to give light. The external quantum efficiency (EQE) is one of parameters used to indicate the light output efficiency of PLEDs, which is defined as the ratio between the number of injected electrons to the number of emitted photons.

In single-layer devices, it is hard to reach balanced charge injection and therefore get high EQE, because the conjugated polymers are mostly hole transporting. Balanced charge injection can be achieved by preparing multiple layer devices with proper geometry, where electrons and holes are injected into the electron and hole-transporting layers, respectively, and transported efficiently to the recombination sites, resulting in light.
Optimization of charge injection has also been done by modifying an electrode to decrease the injection barrier, by using a metal with a low work function as electrodes or inserting a thin alkali fluoride or alkali chloride, such as lithium fluoride or sodium chloride between the active layer and the metal electrode.\textsuperscript{91-93}

### 5.2 Molecularly-doped PLEDs

One crucial aspect that limits the EQE of PLEDs is the formation of excited states. From quantum mechanics, injection of charges into the active polymer layer of PLEDs leads to both singlet and triplet excited states, with a ratio of 1:3.\textsuperscript{15} In reality, however, the ratio of singlets to triplets may be related to a material’s and device’s properties.\textsuperscript{14,94} It is generally agreed, however, that both the singlet and triplet excited states are formed near 1:3.\textsuperscript{94,95} Only transition from singlet excition to the ground state is allowed, giving rise to photons. The transition from the triplet to the ground state is forbidden, following spin conservation of quantum mechanics’ rules. If nothing is done to harvest the triplet excited states, they are lost in non-radiative relaxation, guaranteeing a reduced light output efficiency.

Doping a heavy metal complex guest into a polymer host in a PLED may overcome the above limitation.\textsuperscript{96} In the ideal case (see Fig. 5.2), the energy levels of the singlet and triplet states of the polymer host should be higher than that of the metal complex, making the energy transfer from the polymer host to the metal complex guest favorable. The heavy metal-induced spin-orbit coupling breaks spin conservation rules and allows the transition from both singlet and triplet excited states to the ground state to occur through radiative emission, resulting in electrophosphorescence.

Intensive research on electrophosphorescence started by doping metal complexes into small organic molecules to prepare LEDs\textsuperscript{97} in 1998. This field then turned to polymer-based LEDs\textsuperscript{98,99} where polyvinylcarbazol\textsuperscript{99}, its derivatives\textsuperscript{100} and polyfluorene derivatives\textsuperscript{99,101} were used as a polymer host.
Increased EQE values up to 20% were demonstrated\textsuperscript{96}. Furthermore, these early works improved understanding of energy transfer mechanisms and exciton formation at the guest and led to efficient white light LEDs\textsuperscript{100,102}.

In the following electroluminescence, including electrofluorescence and electrophosphorescence, energy transfer types, and the formation of excited state at metal complex sites are described.

1. Fluorescence and electrofluorescence (EF)

The radiative transition from a singlet excited state ($S_1, S_2, \ldots$) to the ground state ($G$) is called fluorescence. If the singlet state is electrically excited, the radiative decay from the singlet excited state to the ground state is referred to as electrofluorescence.

2. Phosphorescence and electrophosphorescence (EP)

The radiative transition from a triplet excited state ($T_1, T_2, T_3, \ldots$) to the ground state, when the spin conservation rule is broken, is called phosphorescence. Electrically induced phosphorescence is referred to as electrophosphorescence.

\textbf{Fig. 5.2.} Schematic diagram of electrofluorescence (EF) and electrophosphorescence (EP) of radiative transition from the first singlet ($S_1$) and first triplet excited states ($T_1$).
3. Förster energy transfer

Förster energy transfer refers to the non-radiative energy transfer from the singlet ($S_1$) of a polymer host to the singlet ($S_1^*$) of a metal complex guest, $S_1 \rightarrow S_1^*$. It is a dipole-dipole interaction and requires spectral overlap between the emission of the polymer host and the absorption of the metal complex guest. The energy transfer efficiency is inversely proportional to the sixth power of the distance between the host polymer and the complex guest side. Typically the exciton diffusion length is less than 10 nm.

4. Dexter energy transfer

Dexter energy transfer describes the energy transfer from the triplet ($T_1$) of the polymer host to the triplet ($T_1^*$) of a metal complex site, $T_1 \rightarrow T_1^*$. It is an electron-electron exchange interaction between a polymer and metal complex, within which the total spin of the system is conserved. This process occurs when there is a spectral overlap between the phosphorescence emission spectrum of the host and the singlet ground state to first excited state absorption spectrum of the guest. An even shorter separation distance between the polymer host and the metal complex guest favors Dexter energy transfer over Förster energy transfer.

![Diagram of Förster and Dexter Energy Transfer](image)

**Fig. 5.3** Illustration of Förster and Dexter Energy transfer from a polymer host to a metal complex.
5. Electroplex formation

A metal complex guest may also trap charges injected from an electrode. These charges can combine with opposite charges at a neighboring molecule and form an excited state, namely an electroplex\textsuperscript{99,103}. Radiative decay of the excited state can also lead to electrophosphorescence.

6. Triplet-triplet annihilation

Triplet-triplet annihilation is a potential process existing in both the polymer host and the metal complex, which results in singlet excited state formation in the polymer or metal complex. The process in the metal complex is affected by the concentration of the metal complex\textsuperscript{99,102}.

Poly(thiophenes) form another conjugated polymer family, and have been successfully used for fabricating PLEDs that emit light covering the range from violet and visible to infrared. It is noted that the inter-system-crossing yield is higher in general as compared to other polymers due to the heavy sulfur atom\textsuperscript{16}. It is very necessary to harvest the triplet excited state of polythiophene based LEDs in order to enhance performance of this kind of PLED. Our study selected poly(3-methyl-4-octylthiophene) (PMOT) as a polymer host and an iridium or platinum complex as guest to fabricate the molecularly-doped LEDs. Energy transfer from the polymer host to the two kinds of guest and the formation of an exciton at the guest side were studied using photoluminescence and electroluminescence. Our studies showed that energy transfer dominated as the route for exciton formation in the iridium complex containing LEDs. Exciton formation by charge-trapping was involved in the platinum containing LEDs.

PMOT used as polymer host in our work did not have a sufficiently large bandgap, which limited the performance of the molecularly doped LEDs. The study, however, demonstrated a new direction in which polythiophene can be a candidate as a host to realize electrophosphorescence in PLEDs. Large bandgap polythiophenes are required to optimize the performance.
5.3 Polymer solar cells (PSCs)

Polymer solar cells (PSCs) form another conjugated polymer-based group of optoelectronics, which profit well from the development of PLEDs because of the use of similar materials and fabrication technologies. The same reasons as for PLEDs, ease of preparation, low cost, low weight and flexibility of the devices, make the polymer-based solar cells very attractive, although the power conversion efficiency is not as high as that of silicon-based solar cells (10-20 %).

There are number of different types of conjugated polymer-based solar cells: polymer/polymer blends\textsuperscript{104,105}, polymer/polymer double layer\textsuperscript{106}, polymer/fullerene double layer\textsuperscript{107,108}, polymers blended with soluble fullerene derivatives (also called polymer/fullerene bulk heterojunction)\textsuperscript{109,110} and polymer/inorganic hydride\textsuperscript{111,112} solar cells. Amongst PSCs, polymer/fullerene bulk heterojunction solar cells are promising because they have considerably high power conversion efficiency and easiest fabrication. The work in this thesis deals with polymer/fullerene bulk heterojunction solar cells, unless otherwise stated.

5.3.1 Basic working principle

The process of converting solar light into electric current in PSCs is accomplished by the following steps and illustrated in Fig. 5.4.

1. Light (solar photons) passes through a transparent electrode and is absorbed by the active layer (mainly by the polymer), leading to the formation of an excited state (an exciton), \textit{i.e.} a bound electron-hole pair, the electron is in the LUMO and the hole in the HOMO of the polymer.

2. The exciton diffuses to the region where exciton dissociation occurs, for instance, to the interface of the electron donating polymer that has
high ionisation potential and the electron accepting material that has a high electron affinity. The exciton then dissociates into free charges. The electron and hole are transferred to the electron donating and accepting materials, respectively. The driving force for charge separation and transfer, in this case, is the difference in electron affinity or in LUMO levels between two materials at the interface, with the relationship of LUMO$_{acceptor}$ > LUMO$_{donor}$.

(3) Charges are transported under an electric field. These charges might recombine when an electron and a hole are close enough during the transport.

(4) Charges are collected by the two electrodes.

Fig. 5.4. Schematic diagram of the working principle for polymer/polymer or polymer/fullerene bulk heterojunction solar cells. Procedure (1): Absorption of light by the polymer and formation of exciton; Procedure (2): Exciton diffusion and charge dissociation at the interface between the electron donating polymer and the electron accepting material; (3): Charge transport and/or recombination; (4): Collection of charges by the two electrodes.

5.3.2 Characterization of solar cells
The following parameters are important in characterizing the performance of SCs:

(1) Current density-voltage (J-V) characteristics:

- When a SC is in darkness, current is increased exponentially with the application of a forward bias, and almost blocked when a backward bias is applied. This is the rectification property of a diode (see Fig. 5.5), often characterized by the *rectification ratio*, $RR$, given by the ratio of current densities between two applied voltages with the same magnitude but opposite sign.

- When a SC is illuminated, with zero bias (short circuit condition), current flowing in the circuit is pure photo-induced current, namely short circuit current. *Short circuit current density*, $J_{sc}$, is used to characterize the performance of a SC. With increasing applied forward bias, the electric field-induced current (injection current) competes with the photo-induced current and at a certain applied voltage, the two currents cancel each other. This voltage is known as the *open-circuit voltage*, $V_{oc}$. The bandgap between the LUMO of the electron-accepting molecule and the HOMO of the electron-donating polymer has a major effect on $V_{oc}$ while the work function of electrodes has only a weak influence on $V_{oc}$. Due to the complex physical processes, many factors affect $J_{sc}$, such as mobility of charge carriers, the molecular weight of the active materials, morphology of the active layer and the electrodes used.

- For a J-V curve of a diode that is illuminated by light, the ratio of the maximum of the product of $J$ and $V$ to the products of $J_{sc}$ and $V_{oc}$, is referred to as the *fill factor*, $FF$, and reflects the charge transport properties in the diode.

$$ FF = \frac{(J \cdot V)_{\text{max}}}{J_{sc} \cdot V_{oc}} $$
Fig. 5.5. Typical J-V characteristic of a solar cell under the dark and the illumination.

(2) Power conversion efficiency ($\eta_{PCE}$) and incident photons to current conversion efficiency ($IPCE$):

- **Power conversion efficiency**, $\eta_{PCE}$, is defined as the ratio of input light power to the output electric power of the device. It can be determined from the J-V characteristic, and written as

$$\eta_{PCE} = \frac{P_{out}}{P_{in}} = FF \cdot \frac{J_{sc} \cdot V_{oc}}{L_0}$$

- **The incident photons to current conversion efficiency**, $IPCE$ is defined as the ratio between the total number of collected electrons in an electric circuit and the total number of photons incident to a SC. The IPCE is also known as the external quantum efficiency (EQE). It can be determined by measuring the photo-induced current of a SC under illumination from an incident monochromic light under short circuit conditions and is given by:

$$IPCE (\lambda) = EQE (\lambda) = 1240 \cdot \frac{J_{sc}}{\lambda \cdot L_0}$$
where \( J_{sc} \) is the photo-induced photocurrent density in units of \( \mu A/cm^2 \) under short circuit conditions, \( \lambda \) and \( L_0 \) are wavelength and power density of the incident light, in units of nm and Watt/m^2, respectively.

5.4 **PSCs based on low-bandgap polymer**

Polymers with a high absorption coefficient and broad spectra are essential for harvesting solar photons. The latter properties increase the number of converted electrons and the power conversion efficiency. However, most conjugated polymers have a bandgap above 2 eV, and absorb only visible wavelength light, which only accounts for about 40\% of solar irradiation energy (see Fig. 5.6). To use longer wavelength solar photons from solar irradiation, low-bandgap polymers that extend the absorption spectra into the red and infrared regions are necessary.

**Fig. 5.6.** Solar spectrum irradiation (solid line) and solar energy irradiation distribution (dash line) as a function of wavelength. The AM 1.5 Spectrum from American Society for Testing and Material (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation\(^{121}\). The total power density of the irradiance calculated from the spectrum is 90 mW/cm\(^2\). Details can be found in\(^ {121} \).
A consequence of lowering the bandgap of a polymer is an energy level shift in one or both of LUMO and/or HOMO. This might induce energetic mismatch of LUMO levels between electron donating and accepting materials in a SC hence weakening the driving force for exciton dissociation, resulting in a reduction of photo-induced current generation, and making IPCE and $\eta_{IPCE}$ small. This has been shown for some low-bandgap polymers blended with the famous phenyl-C$_{61}$-butyric acid methylester, PCBM, to fabricate solar cells$^{122-124}$, although PCBM has been demonstrated to have very good electron accepting properties when blended with some visible-light absorbing polymers, for example, polythiophene derivatives$^{21,109}$, poly(p-phenylene vinylene) derivatives$^{110,119}$, polyfluorene copolymers$^{125,126}$. Electron-accepting materials whose LUMO levels match that of a low-bandgap polymer are required.

On the other hand, a loss of optical absorption from a low bandgap polymer subjected to visible light maybe another consequence when the absorption is extended to both visible and infra-red wavelength regions. This is the case for some alternating polyfluorene copolymers$^{125-127}$. Properly selecting electron accepting molecules may also compensate for the loss of absorption by electron donating polymers$^{128,129}$.

In this thesis work, we used a series of newly synthesized, novel, low-bandgap polyfluorene copolymers (see Fig. 5.7) as electron donating polymers to fabricate solar cells. A series of fullerene derivatives (see Fig. 5.7) was selected and used as electron accepting materials in SCs, in order to match the energetic LUMO levels between the polymers and the fullerenes.
Fig. 5.7. Chemical structures of a series of polyfluorene copolymers: APFO-Green1, APFO-Green3 and APFO-Green4; and different fullerene derivatives: phenyl-C_{61}-butyric acid methylester, PCBM, 3'-(3,5-Bis-trifluoromethylphenyl)-1'-(4-nitrophenyl)pyrazolino[60]fullerene, BTPF60 and 3'-(3,5-Bis-trifluoromethylphenyl)-1'-(4-nitrophenyl)pyrazolino[70]-fullerene, BTPF70.

The photocurrent responses, EQE, (see Fig. 5.8) in both the near infrared and visible regions were obtained with SCs where the low-bandgap polymers blended with the C70 derivative were used as the active layer. In particular an EQE of ~25% at $\lambda = 400$ nm, 9.4% at $\lambda = 800$ nm and with the onset of current
generation at $l = 1\mu m$ was demonstrated in one of the SCs in the series, exhibiting one of the best results in the field. The $J_{sc}$, $V_{oc}$ and $\eta_{PCE}$ of 3.4 mA/cm$^2$, 0.54 V and 0.7% were obtained for this SC.

**Fig. 5.8.** (a) Absorption spectra of the low-bandgap polyfluorene copolymer APFO-Green1 (solid square), APFO-Green3 (solid square), APFO-Green4 (open triangle) and the fullulene derivative, BTPF70 (solid line) and (b) EQEs of APFO-Green1:BTPF70 (solid square), APFO-Green3:BTPF70 (open circle), APFO-Green4:BTPF70 (open triangle) based devices. The blend ratio between these low-bandgap polymers and BTPF70 is 1:4.
These outstanding properties were attributed to the following:

a. the low-bandgap polyfluorene copolymers whose absorption spectra cover both visible and infrared regions;

![Absorption Spectra](image1)

**Fig. 5.9.** Comparison of (a) absorptions of BTPF70 (open square), BTPF60 (open triangle) and PCBM (solid circle) and (b) EQE of these fullerene blends with APFO-Green1 based devices, where the fullerenes were BTPF70 (open square), BTPF60 (open triangle) and PCBM (solid circle) and the blend ratio between APFO-Green1 to individual fullerene was 1:4, respectively.
b. the energetic match in LUMO levels between the polymers and the C70 derivative, which supplies the driving force for charge transfer;

c. the existence of intermolecular charge transfer\textsuperscript{130-132} between the C70 molecules that contribute to the photocurrent;

d. the contribution from the absorption of the C70 derivative to the current response (see Fig. 5.9) over a certain part of the visible region, which compensates for the loss of absorption of polymers in the region.

These were suggested by studies of optical absorption, photoluminescence quenching and electrochemical determination of LUMO levels of the series of polymers and different fullerene derivatives\textsuperscript{133-135}. 


6. Future outlook

6.1 Increasing aspect ratio of the polymer pattern using thermal reflow

As demonstrated in our paper\textsuperscript{56}, we are able to pattern single and double-layer polymer arrays onto a substrate by surface energy controlled dewetting, especially conjugated polymers on a conducting surface, which is very useful for organic optoelectronics applications. However the aspect ratio of patterns is limited, which makes it hard to meet the requirements for optoelectronics’ applications. A pre-patterned double-layer array that consists of two polymer layers with different glass transition points and proper thickness, might be used to prepare a high aspect ratio array when reflowing\textsuperscript{136} upon annealing.

6.2 Integrating of surface energy controlled patterning techniques into biochips or optoelectronics fabrication

Using a bare stamp to modify the surface energy of a surface is simple and very promising for fabricating biochips for the detection of biomolecules\textsuperscript{137}.

Submicro-scaled polymer stripes prepared using surface energy controlled dewetting have been shown to be able to act as a template and align added polymer molecules orientation, which will be helpful for fabricating conjugated polymer layers which emit polarized light when optically or electrically excited.

6.3 Surface chemical analysis on PEDOT before and after electrochemical doping

Surface energy changes of PEDOT in the forms of VPP-PEDOT and Orgacon (PEDOT:PSS) during electrochemical redox have been explored\textsuperscript{32}. The reason for that may not be only due to the polarization development on the backbone of the polymer and swelling of polymer, but might also be due to the...
surface composition and molecular orientation. Therefore it is useful to analyse the surface chemicals by some surface analysis techniques, for instance photoelectron spectroscopy, IRAS or Raman, in order to fully understand the mechanism of surface energy changes during electrochemical redox in an aqueous electrolyte.

6.4 Carrier multiplication via multiple exection generation in polymer-nanocrystal quantum dot solar cells

One research group in Louisiana Tech University has shown that a quantum efficiency of more than 1 was obtained in a polymer–nanocrystal quantum dot photodetectors. This was attributed to the multiple exection generation in the quantum dot and therefore enhancing the charge carrier generation. This concept is quite interesting and should be used in application of polymer-nanocrystal solar cells because of the similarity of photovoltaic for the both type devices. It is important to understand the mechanism of multiplication of exciton (one photon to more than one excitons), and to know how to efficiently carried out charge separation, transport and ..., in order to construct highly efficient polymer-nanocrystal quantum dot solar cells.
7. Summary of papers

7.1 Surface energy modification and patterning of conjugated polymers

Paper I. PEDOT surface energy pattern controls fluorescent polymer deposition by dewetting. A method of patterning surface energy on surfaces using a bare elastomeric stamp and furthermore patterning a conjugated polymer directly from an organic solution on a conducting polymer surface by surface energy controlled dewetting was invented. The feature sizes of the patterned polymers are in the 10 - 100 µm range. Surface energy modification is due to the transfer of “inks” on the stamp as revealed by infrared reflection absorption spectroscopy. The dynamics of the modification process were characterized by contact angle measurement.

Paper II. Single and bilayer submicron arrays of fluorescent polymer on a conducting polymer surface with surface energy controlled dewetting. For the work in the previous paper we were able to pattern a polymer by spin-coating directly from an organic solution with low vapor pressure and evaporation rate. When an organic solution with a high vapor pressure and evaporation rate, on the other hand, a flat film is formed. In this paper we demonstrated a method of patterning single or double-layer polymers on a PDMS-modified surface upon annealing of the polymer film above its glass transition point.

The influence of pattern geometry and film thickness on the patterned film morphology were studied.

Paper III. In-situ Wilhelmy balance surface energy determination of poly(3-hexylthiophene) and poly(3,4-ethylenedioxythiophene) during electrochemical doping-dedoping. Electrochemical doping of conjugated polymer displays another way of modifying a surface. The dynamic surface
energy changes with doping levels were investigated in-situ with a Wilhelmy balance. Capillary rise has also exhibited the possibility for monitoring in-situ of surface energy changes.

7.2 Opto-electronics devices based on conjugated polymers

Paper IV. Electrophosphorescence from substituted Poly(thiophene) doped with iridium or platinum complex. Converting nonradiative triplet excitons to radiative excitons in PLEDs is the key issue to overcoming the low external quantum efficiency of PLEDs. An increased efficiency can be achieved by doping phosphorescent heavy metal complex into a polymer matrix, because spin-orbital coupling, induced by the heavy metal, breaks the transition rule and allows the triplet exciton to ground state transition occur radiatively, hence enhancing the efficiency. Two metal complexes (Ir and Pt) were doped into a polythiophene based PLED. The energy transfer was investigated with electroluminescence and photoluminescence methods, revealing that complete energy transfer from the polymer matrix to the metal complex in the Ir-containing PLEDs was the main source of the electrolumiscence. In the Pt-containing PLEDs on the other hand, charge-trapping effects also contribute to the electroluminscence.

Paper V. Infrared photocurrent spectral response from a plastic solar cell with low-bandgap polyfluorene and fullerene derivative. Using a low band-gap, conjugated polymer blend with a fullerene to fabricate bulk heterojunction SCs is one strategy for harvesting more solar photons with red and infrared wavelength from solar energy radiation and then to convert the photons into current. Lowering the band-gap results in an energy level shift in one or both of LUMO and/or HOMO levels. This may lead to energetic mismatch in LUMO levels between the polymer and the fullerene and weaken the driving force for charge transfer and thereby make the SCs inefficient. A novel low-band gap polyfluorene copolymer (APFO-Green1) was synthesized and blended with
two different C₆₀-derivates to fabricate SCs. The resulting diodes demonstrated that efficient red and infrared photo-induced current responses can be obtained in diodes where the fullerene LUMO matches that of the polymer. An external quantum efficiency of 8.4% at 840 nm and 7% at 900 nm and the onset of photocurrent generation at 1µm were achieved, which demonstrated one of the best results in the field.

**Paper VI. Enhanced photocurrent spectral response in low-bandgap polyfluorene and C₇₀-derivative based solar cells.** Another consequence of lowering the band-gap of a polymer is the loss of absorption in the visible wavelength, as the absorption of the polymer has been extended to both the visible and infrared wavelength regions. Determination of energy bandgap of the polymer and a C₇₀-derivative by optical absorption and electrochemistry implied that the absorption of the C₇₀-derivative could compensate for the loss of absorption by the polymer. The LUMO of the C₇₀-derivative matches the low bandgap polymer (APFO-Green 1). SCs prepared using the APFO-green 1 as electron donor and the C₇₀-derivative as electron acceptor resulted in an enhanced photocurrent spectral response as compared to that presented in Paper V. The external quantum efficiency of 9.4% at 800 nm and 7% at 900 nm, with the onset of photocurrent generation at 1µm were obtained. The power conversion efficiency of 0.7%, is the best result in the field.

**Paper VII. Polymer solar cells with low-bandgap polymers blended with C₇₀-derivative give photocurrent at 1 µm.** A new series of low-bandgap polyfluorene copolymers with different acceptor-donor–acceptor moieties has been synthesized. The bandgap values of the polymers of 1.2-1.5 eV, were determined using optical absorption and electrochemistry. The LUMO and HOMO varied with the strength of donor-acceptor-donor moieties. These polymers, blended with the C₇₀-derivative used in Paper VI, were used to prepare SCs, which showed promising photovoltaic properties. The spectral
response of the photocurrent covers visible and near infrared wavelength regions with the onset of photocurrent generation extended to 1µm. Meanwhile the correlations of open-circuit voltage of the diodes on the LUMO and HOMO values of the fullurene and the polymers were discussed.
Reference


32. Wang, X., Ederth, T. and Inganäs, O., *in manuscript*.


Ásberg P., Nilsson K.P.R., Ingaäs, O., *Patterning method for biosensor applications and devices comprising such patterns, PCT/SE05/00413*.


85. Wang, X., Tvingstedt, K., and Inganäs O., in manuscript.


http://rredc.nrel.gov/solar/spectra/am1.5/.


