Evaluation of the Process of Solvent Vapor Annealing on Organic Thin Films

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ABSTRACT

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Solvent vapor annealing has recently emerged as an intriguing, room-temperature, and highly versatile alternative to thermal annealing. The chemically selective interaction between solvents and organic semiconductors opens new opportunities to selectively anneal certain components of the device, while leaving others intact. On the downside, these interactions are complex and rather unpredictable, requiring further investigation.

We propose a novel methodology to investigate solvent-film interactions, based on use of an in situ quartz crystal microbalance with dissipation (QCM-D) capability and in situ grazing incidence wide angle X-ray scattering (GIWAXS). These methods make it possible to investigate both qualitatively and quantitatively the solvent vapor uptake, the resulting softening and changes (reversible and/or irreversible) in crystallinity.

Using this strategy, we have investigated the solvent vapor annealing of traditional donor and acceptor materials, namely poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-Phenyl-C61-butyric acid methyl ester (PCBM). We find these materials retain their rigid structure during toluene vapor annealing and do not dewet.

We also investigated the toluene vapor annealing of several newly proposed acceptor molecules (pentacene-based) modified with various silyl groups and electron withdrawing groups to tune the packing structure of the acceptor domains and energy levels at the
donor-acceptor interface. We found a dramatic effect of the electron-withdrawing group on vapor uptake and whether the film remains rigid, softens, or dissolves completely. In the case of trifluoromethyl electron-withdrawing group, we found the film dissolves, resulting in complete and irreversible loss of long range order. By contrast, the cyano group prevented loss of long range order, instead promoting crystallization in some cases. The silyl groups had a secondary effect in comparison to these.

In the last part of the thesis, we investigated the toluene vapor annealing of P3HT-based blends. In general, the blend behavior was strongly affected by the choice of the acceptor. Nevertheless, the polymer mediated the outcome, maintaining the integrity of the blend and preventing dewetting altogether. The TIPS (silyl) substituted pentacene molecules consistently segregated from the blend and crystallized on the surface, revealing their incompatibility with P3HT.
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<td>A</td>
<td>Acceptor</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>D</td>
<td>Donor</td>
</tr>
<tr>
<td>GIWAXS</td>
<td>Grazing incidence wide angle X-ray scattering</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>oDCB</td>
<td>Orthodichlorobenzene</td>
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<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>P3HT</td>
<td>Regioregular poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>PCBDM</td>
<td>[6,6]-Phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
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<td>PV</td>
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I Introduction

1.1 Low-cost organic photovoltaics

The finite supply of traditional energy resources such as oil, coal and natural gas and the detrimental long-term environmental impact of their use have fueled an intense push towards the development of renewable energy resources, both in the Kingdom of Saudi Arabia and beyond. Saudi Arabia, the World’s top exporter of crude oil, sees an urgent need to develop alternative energy resources in order to reduce its own consumption of fossil fuels and to maintain its critical supply to foreign markets.

Photovoltaic technology has been increasingly recognized as an essential component of the future global energy production; it is ideally suited for Saudi Arabia, which is blessed with abundant and consistent solar energy. Although inorganic solar cell technologies account for more than 85% of the current photovoltaics market\(^1\), they are too expensive to be widely utilized. Low-cost solar cell technologies could alter the market dynamics by competing both in material and production cost not only with existing costly Si-based technologies and vacuum-based manufacturing methods, but also with low-cost coal-based electricity generation.

Organic photovoltaic devices made of thin (< 1 \(\mu\)m thick) films of conjugated polymers and molecules on low-cost flexible substrates using low-cost solution processes, such as roll-to-roll and inkjet printing, offer a potential alternative to crystalline Si PV. These organic PV devices could provide electricity at much lower cost if a reasonable
power conversion efficiency (PCE ~10%) and lifetime (~10 years) could be achieved on a large scale.

Organic electronics date back to the 1960s when researchers did fundamental studies on the electronic and optical properties of acenes\(^2\). A key milestone was achieved by Tang in 1986\(^3\), who reporting a single donor-acceptor heterojunction based organic solar cell with PCE = 0.95%. During the 1990s, the development in the understanding, synthesis and processing of semiconducting polymers led to remarkable improvements in fabrication and performance\(^4,5\). In 2009, the record power conversion efficiency stood at just over 6%\(^6,7\), with the most recent record of 8.3% (Konarka) reported in the first half of 2011\(^8\). The remarkable progress of OPV efficiencies since the 1970s puts the community in a position to break the 10% power conversion efficiency within the next few years.

1.2 Principles of operation of an organic solar cell

The mechanism of the operation of organic solar cells exhibits many similarities to their inorganic counterparts, but there are also many important distinctions due to fundamental differences in the organic semiconductors:

1. There is no “band gap” in OPVs and the charge transport in OPVs proceeds by hopping between localized states.

2. The photogenerated excitations, “excitons”, are tightly bound, and the dissociation requires a promotion of energy of around 100meV avoiding radiative recombination.
3. Charge mobilities are very low, but could be compensated by the generally high absorption coefficients.

A typical OPV device is illustrated in Fig. 1.1 (a): The photoactive layer, which contains the electron donor and acceptor is sandwiched between two electrodes - the cathode and the anode, and the sandwiched module is placed on a transparent substrate (glass or plastic). The electrode sandwiched between the photoactive layer and the substrate is required to be transparent and conducting. Most often, a low workfunction metal like aluminum is used for cathode, whereas the anode is a high workfunction transparent conductor, and is usually tin-doped indium oxide (ITO). Two ultra-thin functional layers, named buffer layers, are added between the cathode, anode and photoactive layer and act as hole and electron blocking layers, respectively, while
enhancing electron and hole collection by the respective electrodes\textsuperscript{11,12}. The all-important photoactive layer is discussed after a brief description of OPV device operation.

OPV devices convert light into electric current in four consecutive steps (see Fig. 1.1 (c)): First, photon absorption by the photoactive material (typically the donor) leads to exciton generation by exciting the electrons from ground state in the highest occupied molecular orbital (HOMO) to the excited state in the lowest unoccupied molecular orbital (LUMO). Second, the excitons diffuse in the photoactive layer and those which are generated within reach of the donor-acceptor (D-A) interface are dissociated, with electrons moving into the LUMO level of the acceptor and holes enter the HOMO level of the donor; excitons generated further away from the D-A interface typically recombine and are considered lost. Fourth, the electrons and holes travel to the electrodes through acceptor and donor materials, respectively, and collected by the cathode and the anode, respectively.

Typical solar cell testing relies on current density-voltage (J-V) measurements (see Fig. 1.1 (b)) allow to quantify several key parameters, including the short-circuit current density ($J_{\text{SC}}$), the open-circuit voltage ($V_{\text{OC}}$), the fill factor (FF), and finally, the power conversion efficiency (PCE), which is related to the above parameters as

$$PCE = \frac{FF \times V_{\text{OC}} \times J_{\text{SC}}}{P_{\text{in}}}$$

Equation 1.1,

The $J_{\text{SC}}$ is strongly correlated with the power and spectral characteristics of the incident light, the optical absorption spectrum of the photoactive layer, and the latter’s
ability to move charges to the electrodes for collection. It is critically related to the structural and morphological properties of the photoactive layer, as discussed below. The $V_{OC}$ increases with increasing offsets of the HOMO and LUMO energy levels of the donor and acceptor, respectively, and is one of the key considerations in designing and synthesizing organic semiconductors.$^{13}$

### 1.3 Bulk heterojunction organic solar cells

The photoactive layer is the critical component in a solar cell, because the charge generation and collection occur in this layer. Generally speaking, the architecture of the active layer can be categorized into three types: single layer homojunction, planar heterojunction and bulk heterojunction. The single layer homojunction organic solar cell has the simplest architecture among the different solar cells. The organic semiconductor is sandwiched between the electrodes and generates charge carriers through the electric field produced by the electrodes. Because the exciton diffusion length in organics is typically shorter than 10 nm$^{14}$, all excitons cannot effectively diffuse to the contact if the film is thicker than the exciton diffusion length. This type of structure usually generates PCE < 1%.

The planar heterojunction typically consists of two organic semiconducting layers, a donor and an acceptor sandwiched between the electrodes. Exciton dissociation is located at the D-A interface resulting from the electrostatic forces generated due to the difference
between the HOMO of the donor and the LUMO of the acceptor. The efficiency of the bilayer heterojunction solar cell is greater than the single layer counterpart, because of lower recombination of charge carriers. Gommans\textsuperscript{15} reported a bilayer heterojunction solar cell made by subphthalocyanine (SbuPc):fullerene (C\textsubscript{60}), which has a PCE=3%.

The short exciton diffusion length in organic semiconductors makes both of the planar device architectures unsuitable, for the reason that sufficient light absorption requires film thickness of 100 nm or more short\textsuperscript{16} of a breakthrough in developing extremely high mobility organic semiconductors. These conflicting requirements can be addressed by a different architecture of the photoactive layer, namely the bulk heterojunction (BHJ), wherein the donor and acceptor are blended to form a bicontinuous mixture with nanoscale domains and large D-A interfacial area (see Fig. 1.2), as first proposed in 2001\textsuperscript{17}. The advantages are obvious compared to the planar heterojunction structures. The network structure increases the likelihood that excitons find the D-A interface to split, while the overall thickness allows absorption of many more photons. While the BHJ layer has many advantages, the complexity of forming the correct blend morphology while meeting many other requirements of energy levels is not to be underestimated. It is critical to control the nanoscale phase separation\textsuperscript{18,19}, the continuity of the domains\textsuperscript{20}, the vertical phase separation\textsuperscript{21}, and the crystalline ordering within the donor and acceptor domains\textsuperscript{22}. 
The most commonly studied donor and acceptor materials in BHJ OPV devices are poly(3-hexylthiophene) (P3HT) donor polymer and [6,6]-Phenyl-C61-butyric acid methyl ester (PCBM) small-molecule acceptor, respectively, yielding a PCE approaching 5%\textsuperscript{24}.

### 1.4 Mechanism and affecting factors of solvent vapor annealing process

In an effort to optimize the photoactive layer, the scientific community has focused on two key aspects of organic solar cells. The first is to optimize the phase separation of the blends via solutions process development and post-deposition treatment optimization; the second consists in design and synthesis of new and improved donor and acceptor materials\textsuperscript{25,26,27}.

The processing of the BHJ layer consists of in-production processing (solution processing) and post-production treatments (thermal and/or solvent vapor annealing). The
variables of in-production processing are as following: First, the coating methods\textsuperscript{28} such as spin coating\textsuperscript{29,30}, drop casting or printing techniques. Second, the coating conditions such as spin speed, choice and mixture of solvents, additives, vapor environment and pressure, temperatures of the solution and substrate, surface treatments of the substrate. For instance, different methods of P3HT deposition cause significant differences in the packing structure\textsuperscript{31}, the charge carrier mobility\textsuperscript{32}, and the morphology of P3HT films\textsuperscript{33,34}. In addition, use of high boiling point solvents allows P3HT:PCBM blends more time to phase separate and crystallize during spin-coating\textsuperscript{35,36}. Phase separation during spin coating was monitored \textit{in situ} by Jukes et al.\textsuperscript{37}.

Nevertheless, in-production processing parameters are often not sufficient, and so post-production treatments, such as thermal and solvent vapor annealing are required to achieve the optimal phase separation and crystallinity in the BHJ layer. Post-production treatments of the bulk heterojunction include thermal\textsuperscript{38} and solvent vapor annealing, also known as solvent annealing. Thermal annealing consists in heating the entire sample to a temperature ranging between 80 and 200\textdegree C to promote phase separation, continuity of domains, and crystallization of the various components. While thermal annealing is widespread and quite simple, it anneals the entire sample, including all layers and the substrate, which may cause undesirable mass transport and/or chemical and/or structural changes in other parts of the device.
Solvent vapor annealing has recently emerged as a low-temperature alternative to thermal annealing that can be easily integrated at the end of the in-production process by prolonging the final drying stage. During this time the film crystallizes and phase separates as the film is exposed to small amounts of a solvent, in vapor state, which can soften the material and enable favorable mass transport and phase transformation at room temperature. Solvent molecules interact with the surface of a material and may diffuse into it, depending on solvent-material affinity, permeability of the film and its morphology. The solvent causing intermolecular bonds – typically van der Waals and π interactions between conjugated building blocks – to weaken and for molecules to become mobile, thereby reducing the barrier for the metastable material to self-organize into a more thermodynamically favorable state. In this way, it is similar to thermal annealing without thermally loading the sample or device. Molecules from the solvent vapor can, in principle, be non-interacting or orthogonal with critical organic or inorganic components of the device, making it possible to explore new opportunities to control material characteristics in a targeted manner with unprecedented versatility, while reducing the thermal load applied to other solar cell components.

Despite these advantages, solvent vapor annealing is a complex process that involves mass uptake, unlike thermal annealing, which may result in swelling, delamination and structural damage if not targeted properly. The outcome of solvent vapor annealing depends strongly on the balance of interaction among the solvent, molecules and the substrate. On one hand, when the solvent-molecule interaction is stronger than other
interactions, the molecules are heavily rearranged accompanied with a dewetting process. On the other hand, if the solvent favors both molecules and substrate, the film is moderately modified by the solvent and exhibits slight reorganization\textsuperscript{42}. De Luca \textit{et al.} reported different outcomes of the self-assembly of polymers using different annealing solvents, revealing the effects of polarity and solubility on the crystal formation\textsuperscript{43}. Guo\textsuperscript{44} and Chen\textsuperscript{45} reported that block copolymers can be selectively annealed by using different solvents.

The duration of solvent vapor annealing is also an important factor to take into consideration\textsuperscript{46}. The changes of morphology of bulk heterojunctions with respect to annealing time are reported by many groups to influence the PCE\textsuperscript{47,48}. In Fig. 1.3, we show the time-evolution of surface morphology of hexaazatrinaphthylene (HATNA-2) subjected to chloroform vapor annealing\textsuperscript{40}. It reveals fiber formation after a 10 hour exposure to solvent vapors. Extended solvent vapor annealing can also result in drawbacks. Conboy \textit{et al.} reported dewetting and pin-hole formation following extended solvent vapor annealing of titanyl phthalocyanine:perylene phenethylimide (TiOPc/PPEI) blends, which decreased the performance of devices. Differences in phase separation were also observed in P3HT:PCBM by virtue of increasing the mobility of polymer chains and allowing them to rearrange during solvent vapor annealing, resulting in improved exciton diffusion length.\textsuperscript{49,50} Solvent vapor annealing of P3HT:PCBM blends was found to shift down the LUMO level of P3HT, which facilitates the electron transfer into PCBM domains, and aids exciton splitting. However, excessive phase separation
decreases the exciton’s ability to diffuse to a D-A interface. Therefore, solvent vapor annealing has to be optimized in view of the performance metrics of solar cells, such as the light adsorption, \( J_{SC} \), \( V_{OC} \), PCE, via controlling of the phase separation and microstructure of the donor and acceptor.

Figure 1.3 AFM images of HATNA-2 at different stage of solvent vapor annealing process\(^{40}\).

The interaction of solvent molecules with the conjugated molecules of the semiconductor thin films can be highly selective and depend strongly upon the choice of solvent and chemistry of the conjugated semiconductor. This makes it quite challenging to develop and scale up post-production processing strategies tailored to target materials selectively without first understanding the effects of solvent vapor annealing on the specific molecular thin films. It is also difficult for synthetic organic chemists to know which way to design their materials for ease of processing and post-processing. This is even more critical given the fact that the scientific community seeks to develop new donors and acceptors for high efficiency solar cells.
1.5 The case of solvent vapor annealing of organic semiconductors

Solvent vapor annealing has been reported as a method to modify the P3HT:PCBM bulk heterojunction layer\textsuperscript{51}. The blend morphology, light adsorption, and crystallinity were found to be influenced by solvent vapor annealing, resulting in changes in the PCE, especially when the blend was rich in PCBM. Similar changes were also found by Miller\textsuperscript{47}, wherein the P3HT ordering increased, enhancing the light adsorption between 570 nm to 615 nm, as shown in Fig. 1.4. The increased ordering of the structure was attributed to solvent uptake by the film, which induces more space and higher motility for the reorganization of the polymers\textsuperscript{52}. In addition, solvent vapor annealing of BHJ solar cells consisting of other donors are also reported. Bull reported the effects of vapor annealing of a copolymer solar cell, poly(5,7-bis(3-dodecylthiophen-2-yl)thieno[3,4-b]pyrazine-alt-9,9-dioctyl-2,7-fluorene) (BTTP-F) blended with PCBM\textsuperscript{53}. A 40% increase of the PCE was observed and was attributed to the formation of large crystallites of PCBM during solvent vapor annealing.

Solvent vapor annealing has also been shown to enhance the carrier transport in other organic semiconductors, including triethyilsilylethynyl anthradithiophene (TES ADT)\textsuperscript{54} and dithiophene-tetrathiafulvalene (DTTTF)\textsuperscript{55}. Solvent vapor annealing of block copolymers has also been studied extensively. However, these materials are outside the scope of this thesis.
1.6 Newly developed semiconductor electron acceptors

Recently, the Anthony et al. have demonstrated a broad series of soluble pentacene-based acceptor molecules designed with different functional groups to achieve different packing structures, $\pi$-$\pi^*$ stacking motifs, and energy levels\textsuperscript{56,57,58}, as shown in Fig. 1.5. The various solubilizing silyl groups are used to control the packing structure, ranging from 2D-brickwork, to 1D-slip stacked, to 1D sandwich herringbone, which influences the crystal growth behavior and charge transport direction, while the electron withdrawing groups (trifluoromethyl, cyano, chloro) shift the open circuit voltage. Fig.
1.5 also shows OPV performance when these acceptors are used in solar cells. Although in the same packing motif (e.g., sandwich), the $V_{OC}$ varies with electron withdrawing groups. For example, 2- Cyano-[6, 13]-Bis-(tricyclopentysilylethylene)-pentacene (TCPS-CN-Pn) has a $V_{OC}$ of 0.84 V, whereas 2-Trifluoromethyl-[6,13]-Bis-(trisopropylsilylethynyl)-pentacene (TIPS-CF$_3$-Pn) has a $V_{OC}$ of 0.9 V. The packing motif also appears to be quite critical, as seen in the case of molecules whose design achieves the sandwich structure. In this case, the $J_{SC}$ is 2-5 times greater than the other packing structures.

As these materials are used to test fabricate and test OPV devices, it is critical to understand how the presence of certain side-groups influences phase separation and in particular to understand the extent to which the presence of different functional groups on the acceptor molecule determine their behavior during solvent vapor annealing in pure form or in bulk heterojunction layer.
Currently, there are no reports evaluating the influence of solvent vapor annealing on materials with different chemistries\textsuperscript{62}. There are even fewer systematic studies of the mechanisms of solvent vapor annealing \textit{in situ}\textsuperscript{41}.

1.7 Solvent vapor annealing in this thesis

In this thesis, we develop a new methodology based on the well-known quartz crystal microbalance with dissipation (QCM-D) and complementary \textit{in situ} synchrotron-based X-ray diffraction measurements, to measure the rate and amount of solvent vapor uptake, the resulting changes in viscoelastic properties of the films (softening and/or dissolution), and packing structure and crystallinity. We focus on the well-known cases of P3HT, PCBM, and P3HT:PCBM blends and investigate the influence of solvent vapor annealing on small molecule acceptors developed by Anthony \textit{et al.} (see Fig. 1.5) and modified with different solubilizing and electron-withdrawing functional groups. These experiments are complemented with atomic force microscopy (AFM) and optical microscopy to evaluate the morphological changes of the films.

After a detailed description of materials, processes, and characterization methods, including the \textit{in situ} QCM-D and \textit{in situ} grazing incidence wide angle X-ray scattering (GIWAXS) methods in Chapter 2. We present the solvent vapor annealing behavior of various acceptor thin films in different solvents in Chapter 3. In Chapter 4, we present the
behaviors and morphological changes of bulk heterojunctions of P3HT and several drop-in acceptors. We conclude in Chapter 5.
II Experimental methodology

2.1 Materials and Preparation

2.1.1 Materials

Regioregular poly(3-hexylthiophene-2,5-diyl) [P3HT, (C\textsubscript{10}H\textsubscript{18}S)\textsubscript{n}, molecular weight M\textsubscript{w} = 87 kDa and regioregularity RR = 98.5%; Sigma-Aldrich Co.] and [6,6]-Phenyl-C61-butyric acid methyl ester [PCBM, C\textsubscript{72}H\textsubscript{14}O\textsubscript{2}, 99.5%; American Dye Inc.] were used in this work as reference donor and acceptor materials, respectively.

The chemical structure and packing motif of P3HT are shown in Fig. 2.1. The backbones pack parallel to each other with the $\pi$-$\pi^*$ stacking and the long alkyl chains perpendicular to the backbone and to each other. The lamellar spacing is approximately 1.68 nm\textsuperscript{63}. In thin films, the backbone of P3HT stacks along two main orientations with respect to the substrate plane: face-on and edge-on. The latter one is far more common than the former. The chemical structure of PCBM is shown in Fig. 2.2. PCBM typically forms isotropic close-packed domains.

The molecular and packing structures of the pentacene derivatives investigated in this work are shown in Fig. 2.3. including [6,13]-Bis-(triisopropylsilylthynyl)-pentacene (TIPS-Pn) (C\textsubscript{44}H\textsubscript{54}Si\textsubscript{2}), 2- Cyano-[6, 13]-Bis-(triisopropylsilylthynyl)-pentacene (TIPS-CN-Pn) (C\textsubscript{45}H\textsubscript{53}Si\textsubscript{2}), 2- Cyano-[6, 13]-Bis-(tricyclopentylsilylthynyl)-pentacene (TCPS-CN-Pn) (C\textsubscript{57}H\textsubscript{65}NSi\textsubscript{2}), 2- Trifluoromethyl-[6, 13]-Bis-(triisopropylsilylthynyl)-pentacene (TIPS-CF\textsubscript{3}-Pn) (C\textsubscript{45}H\textsubscript{53}F\textsubscript{3}Si\textsubscript{2}), 2- Trifluoromethyl-[6, 13]-Bis-
(triisobutylsilylethynyl)-pentacene (TIBS-CF$_3$-Pn) (C$_{51}$H$_{65}$F$_3$Si$_2$), and 2-Trifluoromethyl-[6,13]-Bis-(tricyclopentylsilylethynyl)-pentacene (TCPS-CF$_3$-Pn) (C$_{57}$H$_{65}$NSi$_2$). All pentacene derivatives were synthesized by the Anthony group in the Department of Chemistry of the University of Kentucky.

The solubilizing silyl groups (TIPS, TIBS, and TCPS) are the primary means of controlling the packing structure of the acceptor molecules. The primary purpose of the trifluoromethyl and cyano groups is to be electron withdrawing groups controlling the LUMO level of these materials and the open circuit voltage of associated OPV devices, as
previously shown\textsuperscript{61, 62, 63, 64}. The electron withdrawing groups also modify the packing structure as seen in Fig. 2.3.

![Figure 2.3 Single crystal structural motifs of pentacene derivatives investigated in this study.](image)

Acetone (≥99%, Sigma-Aldrich Co.), iso-propanol (anhydrous, 99.5%, Sigma-Aldrich Co.) and ethanol (200 proof, anhydrous, ≥99.5%, Sigma-Aldrich Co.) were used for sample cleaning. Ortho-dichlorobenzene (oDCB) (anhydrous, 99%, Sigma-Aldrich Co.), toluene (anhydrous, 99.8%, Sigma-Aldrich Co.), \textit{n}-hexane (anhydrous, 95%, Sigma-Aldrich Co.), and chloroform (anhydrous, ≥99%, containing amylenes as stabilizer, Sigma-Aldrich Co.) were used for sample preparation and solvent vapor annealing. The physical properties of solvents used for vapor annealing are summarized in Table 2.1. The
known solubility of some of the pentacene derivatives in these solvents are presented in Table 2.2.

Table 2.1 Physical properties of the solvents

<table>
<thead>
<tr>
<th>Name</th>
<th>Toluene</th>
<th>Chloroform</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature (°C)</td>
<td>-93</td>
<td>-63.5</td>
<td>-95</td>
</tr>
<tr>
<td>Boiling temperature (°C)</td>
<td>110.6</td>
<td>61.2</td>
<td>69</td>
</tr>
<tr>
<td>Vapor pressure (Torr at 20 °C)</td>
<td>50</td>
<td>158</td>
<td>121.26</td>
</tr>
<tr>
<td>Viscosity (mPa·s at 20 °C)</td>
<td>0.590</td>
<td>0.58</td>
<td>0.294</td>
</tr>
<tr>
<td>Solubility Parameters ((cal/2cm$^{3/2}$)</td>
<td>8.91</td>
<td>9.21</td>
<td>7.24</td>
</tr>
</tbody>
</table>

Table 2.2 Solubility of pentacene derivatives in various solvents, as measured by the Anthony group

<table>
<thead>
<tr>
<th>Solubility (wt %)</th>
<th>Toluene</th>
<th>Hexane</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPS-Pn</td>
<td>5</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>TIPS-CN-Pn</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIPS-CF$_3$-Pn</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIBS-CF$_3$-Pn</td>
<td>17.5</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>TCPS-CF$_3$-Pn</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.1.2 Sample preparation

The PCBM solution in oDCB (1 wt.%) was prepared by stirring in the dark for 24 hours (SUPER-NUOVA Stirring Hot Plate, Barnstead international Co.) at 250 rpm at room temperature (20°C). Solutions of pentacene derivatives (TIPS-Pn, TIPS-CN-Pn, TIPS-CF$_3$-Pn, TIBS-CF$_3$-Pn, TCPS-CN-Pn, and TCPS-CF$_3$-Pn) were prepared in toluene (1 wt. %) at room temperature (20°C). The P3HT solution in toluene (1 wt. %) was prepared by stirring in the dark for 24 hours on a hot plate at 250 rpm and 50°C, followed by cooling to room temperature prior to spin-casting. The P3HT:Pn solutions (P3HT:TIPS-Pn, P3HT:TIPS-CN-Pn, P3HT:TIPS-CF$_3$-Pn, P3HT:TIBS-CF$_3$-Pn, P3HT:TCPS-CN-Pn, and P3HT:TCPS-CF$_3$-Pn) in a toluene:oDCB (volume ratio 7:3) solvent mixture (1 wt. %) were prepared by stirring in the dark for 24 hours on a hot plate at 250 rpm and 50°C, followed by cooling to room temperature prior to spin-casting.

We used two kinds of substrates, Si wafer covered with 300nm thermally grown SiO$_2$ and substrates consist of 14 mm diameter quartz crystal sensors coated with Au on each side and terminated with a SiO$_2$ layer. The substrates were cleaned according to the following procedure:

1. Exposure to UV-ozone (UV-Ozone ProCleaner™ Plus, BioForce Nanosciences Co.) for 10 mins to remove organic contaminations.

2. Sonicate in ultrasonic bath (2510-R MTH, Bransonic Co.) for 5 minutes in the following solvent: acetone, iso-propanol, and ethanol, consecutively.
3. Rinse with deionized water and dry in pure N₂ flow.

4. Exposure to UV-ozone again for 5 mins for final decontamination and to achieve reproducible hydroxylation of the SiO₂ surface.

Organic thin films were spin-cast (SPIN150- NPP, SPS-Europe) on the quartz crystal sensors by dispensing 100 µl solution and immediately spinning the solution at 200 rpm for 5 s followed by 1000 rpm for 40 s. An acceleration of 2000 rpm/s was used for all spin-coating experiments.

### 2.2 Quartz Crystal Microbalance with Dissipation (QCM-D)

#### 2.2.1 Introduction

Quartz crystal microbalance with dissipation (QCM-D) is an extension of the traditional QCM technique, wherein a piezoelectric crystal’s resonance frequency decreases with increasing mass of, e.g., a thin film deposited via vacuum evaporation or sublimation. The QCM-D can monitor mass change in real-time, as well as evaluate the viscoelastic properties of the deposited mass, thus making it sensitive to the thickness of a film as well as its structure and processes, such as adsorption and phase transformation.

The piezoelectric effect in quartz crystals can be induced by an applied electric field. Thus, when a quartz crystal is placed in an alternating electric field with a given certain frequency, the quartz crystal mechanically oscillates. By using an electronic resonator and
AT-cut angle quartz crystal, stable operation can be achieved at room temperature\textsuperscript{65}. Sauerbrey\textsuperscript{66} reported a linear relationship between the frequency and the mass bound to the crystal (see below), which subsequently led to the QCM being widely adopted as the preferred \textit{in situ} thickness and rate measurement technique for vacuum deposition processes.

In the 1980s, solution-based QCM was developed\textsuperscript{67}, expanding the application of this technique to areas such as biotechnology\textsuperscript{68}. However, when QCM is used in detecting mass changes in liquid media, the measured value is not accurate because of the viscous and elastic contributions of the medium to the oscillation of the crystal. Moreover, “soft” media violate the assumptions of Sauerbrey equation, which assumes the adsorbed mass to be rigid. This led to development of the QCM with dissipation measurement capability in 1996, which can detect the damping or the energy dissipation per oscillation period resulting from the viscoelastic character of the materials.

\subsection*{2.2.2 Principle and experimental setup}

A typical QCMD on quartz crystal sensor is shown in Fig. 2.4. As described earlier, the quartz crystal sensor is sandwiched between Au electrodes on each side and terminated with SiO\textsubscript{2} on top. It consists in an AT cut quartz single crystal, which ensures insensitivity of the frequency of oscillations to small temperature fluctuations near room temperature. The circular quartz crystal operates under thickness shear mode of
oscillation at a resonant frequency of 5MHz. The maximum displacements of the crystal vibration occur in the plane of the crystal plate without vertical displacement. Thus, the quartz crystal can be used for liquid-solid applications with minimum damping. In addition, the quartz crystal is sensitive to the structural and mechanical properties of the attached film, including mass loading, liquid-solid and solid-liquid transitions, dissolution, and softening.

![Diagram of quartz crystal and electrode system]

Figure 2.4 Schematic representation of QCM-D operation.

When an alternating current is applied across the electrodes of the sensor near the resonant frequency, the piezoelectric crystal starts oscillating and the mechanical oscillation of a characteristic frequency is produced. There are several separate resonant frequencies (overtones) driving the oscillation in the odd times of fundamental resonant frequency: F1 (~5 MHz, fundamental), F3 (~15 MHz), F5 (~25 MHz), F7 (~35 MHz), up to F15 (~75 MHz), while the viscous penetration depth of the overtones are 250 nm, 150
nm, 100 nm, 85 nm … 60 nm, accordingly. The frequency of oscillations decreases when material attaches to the exposed surface of the crystal, changing its mass by an amount Δm. If the material is rigid, evenly distributed on the surface and much lighter as compared to the crystal, then ΔF varies proportionately to Δm and is related to various overtones by Sauerbrey’s equation. The linear correlation of the frequency and the mass follow is described as follows:

\[ \Delta m = \frac{C}{n} \Delta F \]  \hspace{1cm} \text{Equation (2.1)},

where \( n \) is the harmonic number. \( C \) is defined as follows:

\[ C = \frac{t_q \rho_q}{F_0} \]  \hspace{1cm} \text{Equation (2.2)},

with \( t_q, \ \rho_q, \ \text{and} \ F_0 \) representing the thickness of the quartz crystal, density and resonant frequency, and yielding \( C = 17.7 \ \text{Hz ng/cm}^2 \). The above equations derive from three key assumptions. First, the adsorbed mass should be small compared to the mass of quartz crystal. Second, the adsorption of mass must be “rigid”. Third, the adsorbed mass must be evenly distributed over the sensor. Otherwise, the results are not accurate.

The dissipation of energy in the presence of “soft” layer is related to the viscoelastic properties of the added layer. Dissipation may be measured by monitoring the decay of the oscillation amplitude after switching off the driving power, as shown in Fig. 3.1(b)-(d). The voltage decay shown in Figure 3.1(d) follows an exponentially damped sinusoidal, \( A(t) \):
where $A_0$ is the amplitude at $t = 0$, $\tau$ is the decay time constant, $\varphi$ is the phase, and $F$ is the output frequency, i.e., the difference between the reference frequency ($F_{\text{ref}}$) and the resonant frequency ($F_0$) of the crystal. The dissipation parameter is given by

$$D = \frac{1}{\tau \pi F} \quad \text{Equation (2.4)}$$

$D$ is also defined as follows:

$$D = \frac{1}{Q} = \frac{E_{\text{Dissipated}}}{2\pi E_{\text{Stored}}} \quad \text{Equation (2.5)}$$

where $E_{\text{Dissipated}}$ represents the energy lost during one oscillatory cycle and $E_{\text{Stored}}$ represents the energy stored during the oscillation.

The QCM-D allows a simultaneous monitoring of both $\Delta F$ and $\Delta D$ as well as all overtones thereof to obtain the resonant frequencies $F_1$, $F_2$, … and the corresponding dissipation values, $D_1$, $D_3$ … with a repetition rate of $\sim 10$ Hz. $\Delta F$ can be measured with precision of 0.1 Hz, which is equivalent to a thickness of 0.02 nm in toluene. During analysis, the first overtone is typically omitted as it is very noisy as a result of the small size of quartz crystals used in this study. By probing multiple overtones of frequency and applying a viscoelastic model during data analysis, meaningful information such as mass, thickness, density, viscosity and elasticity of the adhering layer and time-dependence thereof can be obtained during solution processing and solvent vapor annealing.
2.2.3 Data analysis

The QCM-D data evaluation methods consist of three different types: qualitative analysis, quantitative analysis for rigid films and quantitative analysis for soft films. The qualitative analysis can be done from Q-sense raw data, while the quantitative analysis is done using the Qtools software. The evaluation guideline is shown in Fig. 2.5.

```
Raw data: QSoft data set

Are there high D values in my data?

Yes!

Sauerbrey
No viscoelasticity
Raw data plot

No!

D-f plot
Raw data plot

Are the results within the model assumptions?

Yes!

Viscoelastic model
D-f plot

No!

D-f plot
Raw data plot
```

Figure 2.5 Evaluation guideline for the QCM-D data.

Looking at the raw data, if ΔD shift is small compared to ΔF shift, and the overtones have an identical behavior in frequency and/or dissipation, the film is considered rigid and the Sauerbrey model presented above can be used to provide quantitative information, such as mass and thickness.

If the ΔD shift is large as compared to the ΔF shift (ΔD/ΔF >0.2 in experience), and the overtones of frequency and dissipation begin spreading, then the film is soft and the viscoelastic model is required to estimate the properties of the film. The Voigt model is the commonly used viscoelastic model. It consists of a combination of a dash and a spring in parallel. The adsorbed “soft” layer is denoted by a frequency-dependent complex shear
modulus, $G^*$, where the real part $G'$ is the energy storage (storage modulus) and the imaginary part $G''$ is the energy dissipation (loss modulus):

$$G^* = G' + iG'' = \mu_f + i2\pi F\eta_f$$  \hspace{1cm} \text{Equation (2.6)}$$

Assumptions of the Voigt model include the requirement that the quartz crystal is purely elastic, while the surrounding environment is purely viscous and Newtonian. The thickness and density of the film are considered as constant and the shear modulus and viscosity are frequency independent. Further, it is assumed that there is no slip between the adsorbed film and the quartz crystal.

![Diagram of the system modeled by Vogit-model.](image)

**Figure 2.6** Diagram of the system modeled by Vogit-model.

Fig. 2.6 illustrates the ideal system for the Voigt-based model. $\Delta F$ and $\Delta D$ are a function of the shear viscosity of the film ($\eta_f$), the density of the film ($\rho_f$), the elastic shear modulus of the film ($\mu_f$), the thickness of the film ($h_f$), the viscosity of the bulk fluid ($\eta_0$), and the density of the bulk fluid ($\rho_0$).
2.2.4 QCM-D measurements and analysis in our work

In our experiments, we investigate kinetic changes of the film during solvent vapor annealing using the QCM-D as a sensor of solvent vapor uptake and structural changes to the attached thin film. The QCM-D measurements were done using a Q-sense E4 system equipped with QSX 303 crystal sensor (Silicon Dioxide, 50 nm) and a flow module, QFM 401 chamber. The flow module is mounted inside a custom built chamber shown in Fig. 2.7. The chamber consists of N₂ gas inlet and outlet, as well as a reservoir to hold solvent liquid for solvent vapor experiments. A pre-coated crystal sensor is placed in the center of the chamber in ambient air. The temperature of the crystal is fixed at 21°C. Once the microbalance is operated, ΔF and ΔD stabilize, reset to zero, and the experiment may begin. 40 μL of solvent (e.g., toluene) is injected into the reservoir in the sealed chamber. Data is recorded until ΔF and ΔD reach a new equilibrium state, upon which time the solvent vapor annealing process is terminated by removing the cover of the chamber.

Figure 2.7 Solvent vapor annealing in a custom-built environmental chamber built on top of a QCM-D open module.
Qualitative analysis requires that we know the baseline of the solvent liquid on the crystal, \textit{i.e.}, the extreme case when the film dissolves into the solvent, and the other one is the mass of the thin film on the crystal. Combining the raw data from Q-sense software and the baseline measurements, we can determine the state of the organic film on the crystal during solvent vapor annealing.

The solvent liquid baseline can be measured first by dropping 200\,\mu l of solvent on the bare crystal, making sure the crystal is completely flooded and covered by the bulky solvent. In Fig. 2.8, the solid green line represents the changes of \(\Delta F\) and \(\Delta D\) of the bare crystal when the solvent liquid is dropped on the bare crystal. \(\Delta F\) decreases immediately and stabilizes to a steady-state value. Simultaneously, \(\Delta D\) increases as the liquid causes significant energy dissipation. The red lines represent the same situation, but when solvent is dropped on a crystal coated with a soluble film. In both cases, the stabilized \(\Delta F\) and \(\Delta D\) are identical upon dissolution of the film into a large volume of solvent, and regarded as the liquid baseline of the solvent.

Prior to starting solvent vapor annealing, the mass of the thin film on the sensor is unknown; it can only be determined by sacrificing it after solvent vapor annealing is complete by dissolving the entire film by dropping 200 \,\mu l of solvent on the coated QCM crystal. Since this prevents additional experiments, such as AFM, from being performed, it is only done in some cases. Upon dropping the solvent on the soluble film, the frequency shifts towards that of the pure bulk liquid, and the offset (positive or negative)
allows to measure the $\Delta F$ associated to the rigid film. If the $\Delta F$ associated to the solid film is greater than $\Delta F$ of the liquid, as the red dash line shown in Fig. 2.8, then the solvent vapor annealing process can be monitored qualitatively by simply observing the sense of change of $\Delta F$ during solvent vapor annealing. Decreasing $\Delta F$ is unambiguously related to mass uptake of solvent, whereas increasing $\Delta F$ indicates film dissolution. If $\Delta F$ of the solid film is higher than the bulk liquid level of the film decreases during solvent vapor annealing, as the blue dash line shows in Fig. 2.8, then the situation is more complicated, because pure mass uptake cannot be directly distinguished from dissolution when $\Delta F$ approaches the liquid baseline. In this case, the solvent vapor annealing should be analyzed by combing other factors such as the spreading of overtones, the shape of the $\Delta F$ and $\Delta D$ curves and the ratio of $\Delta D$ over $\Delta F$.

Figure 2.8 Illustration of the effects of solvent vapor annealing process with knowledge of $\Delta F$ offsets associated to the liquid solvent, the bare crystal, and the as-deposited thin film on the quartz sensor.
The solid red line in Fig. 2.8 also illustrates the method for evaluating solvent vapor annealing. In accordance with the Sauerbrey equation, decreasing $\Delta F$ indicates solvent uptake by the film, while increasing $\Delta F$ means its dissolution. A slight increase of $\Delta D$ means the film remains rigid, whereas larger increase of $\Delta D$ indicates softening or dissolution of the film. If $\Delta D/\Delta F > 0.2$, the film is considered soft or viscoelastic. The spreading of the overtones of $\Delta F$ and $\Delta D$ also indicate a transformation of the film from rigid to soft. Combining all the parameters, a few of processes can be evaluated as follows:

- If $\Delta F$ decreases without spreading of overtones and $\Delta D$ remains constant, the film is taking up mass without changing its rigidity.
- If $\Delta F$ decreases and $\Delta D$ increases with $\Delta D/\Delta F > 0.2$ and the spreading of overtones of $\Delta F$ and $\Delta D$, the film is taking up mass with softening of the film.
- If $\Delta F$ increases and $\Delta D$ increases significantly and the overtones of $\Delta F$ and $\Delta D$ spread, the film is dissolving to the liquid phase.

With respect to quantitative analysis, the equivalent thickness of the adsorbate the rate of uptake before the film becomes soft are calculated by the Sauerbrey model and fitted by Origin. The Voigt model was not applied in this work, because of the complicated nature of phase transformation in thin films during solvent vapor annealing process.
2.3 Grazing Incidence Wide Angle X-ray Scattering (GIWAXS)

Grazing incidence wide angle X-ray scattering (GIWAXS) is a powerful method for characterization of the packing structure, microstructure, and texture of thin films. Moreover, combined with other measurements, GIWAXS can reveal important characteristics, such as solid-liquid transitions, crystal reorientation, during thermal annealing or solvent vapor annealing.

![GIWAXS geometry](image)

Figure 2.9 GIWAXS geometry.

Fig. 2.9 schematically shows the geometry of a typical GIWAXS experiment. The X-ray beam hits the surface with a fixed angle of incidence $\alpha_i$ which depends on the system under investigated. In our work, the angle of incidence $\alpha_i$ is chosen as $0.15^\circ$, because it is between the critical angle of the thin film material and the substrate. Hence, the thin film is penetrated totally by the X-rays, leading to more complete information about the structure and orientation of the organic thin film.
All the X-ray diffraction abide the Bragg’s law, given by the equation as follow:

\[ n\lambda = 2d \sin \theta \]

Equation (2.7),

where \( n \) is a integer, \( \lambda \) is the wavelength of the X-rays, \( d \) is the spacing of the planes in atomic lattice, \( \theta \) is the half of \( 2\theta \), which is the angle between the incident and reflected beam. In the situation of incidence, the Bragg equation works, too. The X-rays are scattered by atoms in the sample and fly out with a horizontal scattering angle \( \Psi \) and an exit angle \( \alpha_i \). The scattered beam is collected by the area detector, forming a two-dimensional scattering pattern along the horizontal and vertical directions.

Figure 2.10 GIWAXS images in two extreme cases: (a) parallel lamella and (b) perpendicular lamella and a mediate case (c) disordered or partial ordered lamella.

There are two extreme cases to explain the correlation between the structure and the scattering pattern. One case is the parallel lamellae structures; the other one is the vertical lamellae structure. When X-rays penetrate through the parallel lamellae, the scattered pattern is along the \( q_z \) direction with bars of intensity, as shown in Fig. 2.10 (a). When
X-rays penetrate through the vertical lamellae, the pattern shows rod-like shapes normal to the horizon, as shown in Fig. 2.10 (b). For a mediate situation, when the structure is disordered or partial ordered lamella, the diffracted spots are arc along as shown in Fig. 2.10 (c), where the ring is known as Debye-Scherrer rings.

![Crystal lattice](image)

Figure 2.11 GIWAXS image for crystal lattice.

However, the patterns are more complicated in organic small molecule thin films which crystallize into polycrystalline structure instead of lamellae. Thus, these crystal lattice scatters X-rays in both in- and out-of-plane directions. A typical pattern of organic small molecule thin films with crystal lattice is shown in Fig. 2.11. The out-of-plane peaks are marked by (001), (002) and (003).

Fig. 2.12 illustrates the GIWAXS image of a TIPS-Pn thin film. Based on the peaks observed on the detector, the crystal packing orientation, the unit cell dimensions, and the mean crystal size can be deduced
Figure 2.12 (a) GIWAXS pattern of the TIPS-pn spin-cast film, indexed in in- and out-of-plane directions.

(b) The TIPS-pn packing structure on Si wafer in side view.

In our work, the GIWAXS patterns were collected at D-line at Cornell High Energy Synchrotron Source (CHESS) in Cornell University. A wide band pass (1.47%) double-bounce multilayer monochromator supplied an intense beam with the wavelength of 1.23 Å. Si wafer was mounted in a chamber with two Kapton® windows on a sample goniometer with the grazing incident angle of 0.15°, as shown in Fig. 2.13. The Kapton® windows can seal the chamber to achieve stable vapor pressure in the annealing process. An accurate calibration of the incident angle was performed by measuring the x-ray reflectivity from the substrate using an ion chamber. Continuous GIWAXS patterns were collected every 6s with the exposure time of 1s by an area detector (Medoptics) with a pixel size of 46.9 microns and a total area of 50mm × 50mm at a distance of 92.1mm from the sample. A 1.5mm wide tantalum rod was used to block the intense scattering in the low angle of the incident plane.
2.4 Additional methods

A stereomicroscope (Stemi 2000 with AxioCam MRc5 digital microscope camera, Zeiss) was used to image the large-scale features of the surface.

Atomic force microscopy (AFM, the Agilent Technologies 5400 Scanning Probe Microscope, in tapping mode) was performed in tapping mode with a silicon cantilever (nominal spring constant 1.2-29 N/m and resonant frequency 76-263 kHz, Nanosensors Company) to characterize the surface topography and root mean squared (RMS) surface roughness of the film surface.
III Solvent Vapor Annealing of Small-Molecule Organic
Semiconductor Thin Films

In this chapter, we investigate the solvent vapor annealing of acene-based acceptor molecules chemically modified with different functional groups, as shown in Fig. 2.3, to achieve different bulk heterojunction morphologies and D-A interfacial energy band offsets.

In the first part, we investigate the influence of toluene vapor annealing on TIPS-Pn and the classic PCBM. In the second part, we compare the effect of trifluoromethyl- and cyano- terminated molecules and classify their behaviors, followed by the influence of the different silyl solubilizing groups. In the last part, we evaluate the influence of different solvent vapors (toluene, hexane and chloroform) on thin films of TIPS-Pn and TIBS-CF$_3$-Pn.

3.1 Solvent vapor annealing on TIPS-Pn and PCBM Films

In Fig. 3.1 we show the time-evolutions of $\Delta F$, $\Delta D$ and equivalent thickness of solvent uptake (assuming a continuous solvent layer) when toluene vapor annealing TIPS-Pn [(a)-(c)] and PCBM [(d)-(f)] thin films. The process starts as soon as 40μl of solvent is introduced into the sealed chamber, and ends when N$_2$ gas is flown through the chamber at high rate to flush out the solvent vapor.
In the case of TIPS-Pn (left panels in Fig. 3.1), both the ΔF and ΔD change during the process, as seen in (a) and (b), respectively. In the first 100 s of the process (region 1), the three overtones of ΔF decrease simultaneously with matching values, while ΔD remains near zero, suggesting that this regime is dominated only by vapor uptake and that the film remains rigid as per the quartz sensor. As ΔF continues to decrease towards -130 Hz (region 2), ΔD increases towards 10-20 and its overtones split, along with slight splitting...
of ΔF overtones. This suggests that the solvent uptake influences the viscoelastic properties of the film and softens it. Softening is very mild, as ΔD/ΔF < 0.2, which implies the Sauerbrey equation (2.1) is valid throughout the process allowing us to calculate the solvent vapor uptake in terms of equivalent toluene thickness, assuming a mass density of 860 kg/m³ [see Fig. 3.1(c)]. The thickness of the solvent film reaches ~25nm by the end of the process, which can be described well by a modified exponential decay curve with a characteristic time of ~234 s. The initial rate of solvent vapor uptake (region 1) is equivalent to a 0.1 nm/s deposition rate. The process ended abruptly (region 3) and QCM-D measurement reveals the solvent is removed immediately from the film, which recovers its rigidity in full as both ΔF and ΔD recover to their initial values in a matter of seconds.

In Fig. 3.1(d) and (e), we show the changes of the overtones of ΔF and ΔD, respectively, for PCBM thin films during toluene vapor annealing. The entire process is similar to that of TIPS-Pn film, including in the amount of solvent uptake, with the exception that a significant difference is observed in ΔD, which is nearly three orders of magnitude lower than TIPS-Pn at maximum solvent uptake. This indicates that PCBM takes up toluene without any softening. This may be due to the fact that PCBM is not very soluble in toluene. Nevertheless, the Sauerbrey analysis in region 1 reveals a rate of uptake of 0.27 nm/s, which is nearly three times greater than TIPS-Pn. This suggests that solvent uptake is not always related to solubility. The shapes of the ΔF and solvent uptake curves in regions 2 for both TIPS-Pn and PCBM appear to confirm a difference; the
initial high rate of solvent uptake in PCBM appears to subside rather quickly, reaching a maximum thickness of 20 nm as compared with 25 nm for TIPS-Pn. This suggests that solvent uptake is initially mediated by solvent-surface interactions, while subsequent uptake depends on solvent-bulk interactions, which could alter the viscoelastic properties of the film, as indicated by relative softening of TIPS-Pn.

Figure 3.2 The [(a), (b)] GIWAXS and [(d), (e)] AFM images of TIPS-Pn film (left) before and (right) after solvent vapor annealing, respectively. (c) Integration of (001) peak of the in situ GIWAXS of TIPS-Pn film

We have used in situ GIWAXS to monitor the micro-structural changes of caused by toluene vapor annealing the polycrystalline TIPS-Pn film. Similar measurements for PCBM are not meaningful, because it is amorphous in as-cast thin film form. As shown in Fig. 3.2 [(a), (b)], the diffraction peaks observed before and after annealing remained qualitatively unchanged, indicating that no change in the packing structure of TIPS-Pn. However, monitoring the intensity of the (001) diffraction peak [Fig. 3.2 (c)] reveals a
rapid and 5-fold increase in the intensity during the first 100 s of the process, suggesting improved crystallinity and texture in the film during. Subsequent annealing (corresponding to region 2) reduced the diffraction intensity of the (001) peak. The latter did not recover at the end of the process, indicating an optimum process window for vapor annealing this material.

AFM images [Fig. 3.2 (d), (e)] taken before and after the full process reveal dramatic morphological changes. The as-spun film appears relatively flat and continuous with fine features, while the film treated for 400 s reveals large, isolated, rectangular crystallites on the bare Si surface, indicating that the process results in significant crystallization and dewetting. In particular, dewetting of the film suggests that the solvent-film interactions are far stronger than solvent-substrate interactions. The solvent-surface (region 1) and solvent-bulk (region 2) interactions cause dramatic mass transport and rearrangement of the film, which are likely occurring during region 2, where softening of the film suggests it can reorganize towards a thermodynamically favorable structure.

3.2 Solvent vapor annealing of CF$_3$-terminated pentacene derivatives

We now turn our attention to pentacene-derivatives terminated with the trifluoromethyl group (carbon 2 position of pentacene) to investigate their influence on the solvent vapor annealing process. In Fig. 3.3, we plot the overtones of $\Delta F$ [(a), (d), (g)] and $\Delta D$ [(b), (e), (h)] for TIPS-CF$_3$-Pn, TIBS-CF$_3$-Pn and TCPS-CF$_3$-Pn, respectively,
during toluene vapor annealing. The general trends of ΔF and ΔD in this group of materials are consistent with a rapid and significant solvent uptake during the first 10-20 s (region 1) without any detectable structural changes. This is followed by region 2, where ΔD increases quite dramatically and ΔF turns around and increases while overtones are split. This behavior indicates loss of sensed mass, as the film gradually dissolves and liquifies and the quartz crystal does not sense the mass as being coupled to the surface any longer at high frequencies of shear oscillation (>5 MHz). As soon as the chamber is flushed with N₂, both ΔF and ΔD recover in full.

Figure 3.3 The change of [(a), (d), (g)] ΔF, [(b), (e), (h)] ΔD and [(c), (f), (i)] thickness of the TIPS-CF₃-Pn, TIPS-CF₃-Pn and TCPS-CF₃-Pn films, respectively, during toluene vapor annealing.

Comparing the behavior of CF₃-terminated pentacenes to TIPS-Pn, we find that the CF₃ group plays a major role in mediating the vapor annealing process, whereas
substitution of the TIPS groups with TIBS or TCPS has – comparatively speaking – a secondary role.

By linearly fitting the thickness changes in rigid film regime, the rate of solvent vapor uptake is found to be 1.38 nm/s, 1.54 nm/s and 0.33 nm/s for molecules with TIPS, TIBS, and TCPS groups, respectively. For TCPS-CF$_3$–Pn films, ΔF decreased to -300 Hz before turning around and increasing and before the overtones split apart. This comparison suggests that TCPS-substituted pentacenes are more resistant and less prone to structural changes than TIPS- and TIBS- substituted pentacenes. The similar behavior of TIPS- and TIBS-substituted pentacenes is probably due to the fact that both silyl groups (propyl and butyl) are in fact CH$_3$-terminated, whereas TCPS is terminated with a much larger cyclopentyl group.

Structural and morphological studies performed on TIPS-CF$_3$-Pn are summarized in Fig. 3.4. The GIWAXS data taken before (a) and after (b) toluene vapor annealing suggest irreversible loss of long range order. In situ GIWAXS (c) also shows how this occurs during the first 100 s of vapor annealing, during which time QCM-D data showed (Fig. 3.3) conclusive evidence of thin film dissolution. The AFM images collected before (d) and after (e) show that the initially flat films with very low surface roughness (0.575 nm) and fine features is completely transformed. Optical micrographs also reveal macroscopic aggregates formed after the process, which indicates significant macroscale mass transport and reorganization, only possible by liquifying the film.
Figure 3.4 The [(a), (b)] GIWAXS, [(d), (e)] AFM and [(f), (g)] optical microscopy images of TIPS-CF$_3$-Pn film before (left) and after (right) toluene vapor annealing, respectively. (c) Time-evolution of the (001) diffraction peak of TIPS-CF$_3$-Pn film calculated from in situ GIWAXS.

For comparison, in Fig. 3.5, we show the behavior of TIBS-CF$_3$-Pn to be very similar to that of the TIPS-CF$_3$-Pn. Again, the GIWAXS shows that the film loses its long range order and does not recover its crystallinity after dissolving during solvent vapor annealing. However, AFM images show less dramatic morphological changes, suggesting that the material redeposits into a film-like structure at the end of the experiment.

Lack of synchrotron beam time made it impossible to perform a similar study on TCPS-CF$_3$-Pn. However, we expect to see a similar trend in loss of long range order. In Fig. 3.6, we show the optical micrographs of the film before (a) and after (b) the solvent
vapor annealing, significant macroscopic morphological changes hinting at mass transport and dewetting of the film into droplet-like aggregates. This is in agreement with the QCM-D observations that the film softens all the way to a liquid state during solvent vapor annealing.

Figure 3.5 The GIWAXS and AFM images of TIBS-CF₃-Pn film [(a), (d)] before and [(b), (e)] after toluene vapor annealing, respectively. (c) Integration (001) peak of in situ GIWAXS of TIBS-CF₃-Pn film.

It appears that while all CF₃-terminated films dissolve and redeposit at the end of the vapor annealing process, they do not recover their initial long range order. This suggests that while these semiconductors are very sensitive to vapor annealing, their charge transport properties may be negatively impacted by solvent vapor annealing.
3.3 Solvent vapor annealing of CN-terminated pentacene derivatives

In the case of CN-terminated pentacene derivatives, we show in Fig. 3.7 both $\Delta F$ [(a), (d)] and $\Delta D$ [(b), (e)] changes observed during toluene vapor annealing of TIPS-CN-Pn and TCPS-CN-Pn thin films, respectively. In both cases, $\Delta F$ decreases initially without any significant change in $\Delta D$, followed by increase of $\Delta D$ and splitting of the overtones of $\Delta F$, indicating uptake followed by significant softening of the film. The absence of a definitive turnaround of $\Delta F$ similar to what was observed for CF$_3$-terminated molecules indicates that CN-terminated films, while undergoing some localized dissolution, clearly do not liquify. This confirms that the CN group resists solvents more than the CF$_3$ group, but nevertheless results in significantly more softening than for TIPS-Pn.

In Fig. 3.8, we show the changes of crystallinity [(a), (b)] and morphology [(d), (e)] before and after toluene vapor annealing of TIPS-CN-Pn thin films. It can be seen from the GIWAXS images that the films retain their crystallinity after processing. The
time-evolution of the (001) intensity (c) also shows it to decrease only by 10-20% and to remain constant throughout the process, then recovering almost fully at the end of the process.

Figure 3.7 The [(a), (d)] ΔF, [(b), (e)] ΔD and [(c), (f)] thickness of TIPS-CN-Pn and TCPS-CN-Pn film film during solvent vapor annealing, respectively.

This is in sharp contrast to CF$_3$-substituted molecules and even to TIPS-Pn, which did not show a recovery behavior at the end of the vapor annealing process. It indicates that the film retains its long range order, even though we detect significant uptake and softening of the film. Solvent vapor molecules probably interact only with the surface and grain boundaries of the polycrystalline film without dissolving the bulk of the crystallites. From
the AFM images in (d) and (e), we find the film undergoes significant coarsening, but retains a good surface coverage, unlike previous cases of TIPS-Pn and CF$_3$-substituted pentacene derivatives.

Figure 3.8 The [(a), (b)] GIWAXS and [(d), (e)]AFM images of TIPS-CN-Pn film (left) before and (right) after solvent vapor annealing. (c) Integrant (001) peak of in situ GIWAXS of TIPS-CN-Pn film

In Fig. 3.9, we show the changes of crystallinity [(a), (b)] and morphology [(d), (e)] of TCPS-CN-Pn films before and after toluene vapor annealing. The GIWAXS results point to development of significant long range order as a result of vapor annealing. This is confirmed by (c), which shows a steady rise of the intensity of the (001) peak as result of crystallization of the film during toluene vapor annealing. The AFM results show significant aggregation and dewetting of the film, probably because most of the film transforms from amorphous to crystalline.
Figure 3.9 The [(a), (b)] GIWAXS and [(d), (e)] AFM images of TCPS-CN-Pn film (left) before and (right) after solvent vapor annealing. (c) Integrant (001) peak of in situ GIWAXS of TCPS-CN-Pn film.

### 3.4 Influence of functional group

The QCM-D and GIWAXS observations in the case of CN-terminated molecules indicate that significant solvent vapor uptake can simultaneously soften the polycrystalline film while maintaining or promoting crystallization. These findings are in strong contrast with the behavior of CF$_3$-terminated derivatives, which dissolve, liquefy, and do not recover any of the long range order of the as-cast film. The CN-terminated molecules behave more so like TIPS-Pn, which softens mechanically without losing long range order.
The vapor induced liquefaction of the CF$_3$-terminated pentacene films is believed to stem from a very strong affinity between the solvent vapor molecules and the thin film molecules. As all solvent vapors annealing experiments were performed under nominally identical conditions, we can compare, as in Fig. 3.10, the initial rate of solvent vapor uptake of all molecules. The CF$_3$-terminated pentacene films have the greatest rates, followed by CN-terminated pentacene films, and then TIPS-Pn. The slower rate of uptake by TCPS-substituted pentacene suggests that the silyl groups also significantly influence solvent-pentacene interactions.

![Figure 3.10 Initial uptake rates of different films.](image)

In Fig. 3.11, we summarize the influence of the choice of different electron-withdrawing groups (CF$_3$, CN, none) and so-called solubilizing silyl groups (TIPS, TIBS, TCPS) on the toluene vapor behavior of the materials. It is clear that the electron withdrawing groups are of greater consequence than the choice of the silyl groups when it comes to determining solvent-film interactions. Ability to liquefy or retain
solid state during vapor annealing, as well as irreversible loss of crystalline order versus recovery or improvement of crystallinity are of great consequence for organic photovoltaic applications. Loss of long range order reduces the charge carrier mobility and exciton diffusion length in organic semiconductors. It appears that TIPS-Pn and CN-terminated pentacene derivatives can benefit the most from solvent vapor annealing.

![Chemical structures](image)

<table>
<thead>
<tr>
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<td>Softening, crystallization, dewetting</td>
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Figure 3.11 Summary of the influence of the choice of different electro-withdrawing group and soluble silyl groups on the toluene vapor annealing behavior of the materials.
3.5 Solvent vapor annealing using different solvents

Having evaluated the influence of molecular design on the solvent vapor annealing process, and identified TIPS-Pn and CF$_3$-terminated pentacene at the two extremes of toluene vapor annealing behavior, we now evaluate the interaction of different solvent vapors with two molecules: TIPS-Pn and TIBS-CF$_3$-Pn films. In these experiments, we have established the absolute frequency (and mass) associated to the spin-cast molecular film by dropping a large amount of solvent and dissolving the film at the end of the process. This also allows us to identify the liquid baseline of the quartz sensors for easier interpretation of the vapor annealing process, as described in detail in Section 2.1.4. The baseline is regarded as a limit towards which $\Delta F$ and $\Delta D$ will converge upon complete dissolution and liquefying of the film.

In Fig. 3.12, we track by QCM-D the 3$^{rd}$ overtones of $\Delta F$ and $\Delta D$ during the solvent vapor annealing of TIPS-Pn film in toluene, hexane and chloroform solvent vapors. The green, red and blue dash lines represent the baseline of $\Delta F$ in toluene (-310 Hz), hexane (-240Hz) and chloroform (-460Hz) solvents, respectively. The $\Delta F_{\text{film}}$ associated to the as-spun film is below the baseline of chloroform due to its low thickness, but larger than that of toluene and hexane.

As toluene is introduced into the chamber, $\Delta F$ decreases while $\Delta D$ remains near zero, indicating uptake of the vapor while the film remains mechanically rigid, and by extension, in solid state. The $\Delta F$ curve decreases gradually with time and saturates,
indicating that the vapor uptake process saturates. A similar trend is observed when TIPS-Pn is exposed to hexane vapor, with $\Delta D$ keeping close to zero. A different behavior is observed when TIPS-Pn is exposed to chloroform vapor. $\Delta F$ decreases quite significantly at first, followed with a slight turnaround after 400 s exposure. Concomitantly, $\Delta D$ begins to increase after 2-3 minutes and approaches 50, which indicates that the film softens significantly. This indicates that the turnaround of $\Delta F$ is likely due to the film undergoing a solid-liquid transition, resulting in loss of rigid mass from the surface of the quartz crystal sensor. Comparing the solvent vapor annealing behavior of TIPS-Pn films in three different solvents, it appears as the film remains in the solid state despite significant solvent uptake, except in the case of chloroform. These results are interesting, because TIPS-Pn is soluble in all three solvents. However, it appears that chloroform is much more effective at dissolving TIPS-Pn during vapor annealing. This may also be due to the significantly larger vapor pressure of chloroform, which may overwhelm the film. These results are interesting for the fact that all three solvents can dissolve TIPS-Pn in the bulk, but the interaction of their vapors with a thin film is obviously very different.
Figure 3.12 The change of $\Delta F$ and $\Delta D$ during solvent vapor annealing of TIPS-Pn using toluene, hexane and chloroform, in green, red and blue curves, respectively.

We now compare the solvent vapor annealing process of TIPS-Pn to that of TIBS-CF$_3$-Pn in toluene, hexane and chloroform by QCM-D. As shown in Fig. 3.13, the green, red and blue dash lines are liquid baselines for toluene, hexane and chloroform, respectively, indicating that the films in this case are thick enough that the sense of $\Delta F$ change clearly shows whether the material remains solid or dissolves as a result of solvent uptake. The green, red and blue solid lines represent the QCM-D data of the film during vapor annealing by toluene, hexane and chloroform solvents, respectively. As any of the three solvents was introduced in the chamber, $\Delta F$ of the film initially decreased rather rapidly, as compared to TIPS-Pn, while $\Delta D$ increased to around 50, which indicates some softening of the film. Soon after, $\Delta F$ turned around and started moving towards the liquid baseline of the respective solvent. All the while, $\Delta D$ kept rising as well and saturating towards the liquid baseline (not shown). Comparing the solvents among themselves, we
find hexane to be the slowest acting one, while chloroform is the fastest to be taken up and to dissolve the film.

It is interesting to note that hexane vapor annealing appears to dissolve the system fully, as indicated by the convergence of $\Delta F$ towards the liquid level, whereas the others do not appear to do so a priori. However, this may be due to a common artifact of the QCM-D in the presence of liquids, which is a strong dependence of sensed mass upon the wetting/dewetting behavior. If the liquefied film dewets, then the full liquid may not be detected, as the shear evanescent wave in the liquid does not interact with the entire volume of the liquid.

From these room-temperature experiments, it appears that the choice of solvent influences the rate and amount of solvent uptake, making this process very much dependent upon the vapor pressure of the chosen solvent.

![Figure 3.13 The change of $\Delta F$ and $\Delta D$ during vapor annealing of TIBS-CF$_3$-Pn using toluene, hexane and chloroform, in green, red and blue curves, respectively](image-url)
3.6 Conclusion

In this chapter, we demonstrated QCM-D and in situ GIWAXS as a powerful set of techniques to monitor in situ and in real time the solvent uptake and resulting effects on thin film structural and viscoelastic properties. In situ GIWAXS was particularly useful to identify optimal vapor annealing conditions (e.g., for TIPS-Pn), and to reveal which functional groups cause materials to dissolve and prevent materials from recovering their crystallinity after vapor annealing.

In the first part, we investigated the toluene vapor annealing of two well-known materials, namely TIPS-Pn and PCBM. TIPS-Pn film softens when exposed to toluene vapor, while PCBM does not. An optimal vapor annealing window of 100s exists for TIPS-Pn, during which the crystallinity improves. This is followed by a period of decreased crystallinity and softening, during which significant molecular reorganization, mass transport and dewetting modify the thin film into isolated crystallites.

In the second part, we investigated and compared solvent vapor annealing behaviors of pentacene derivatives terminated with different electron withdrawing groups, namely CF$_3$ and CN, and different solubilizing silyl groups, namely TIPS, TIBS, and TCPS. QCM-D analysis reveals conclusively that the electron-withdrawing groups are much more consequential than silyl groups in determining the fate of molecules during solvent vapor annealing. The combination of QCM-D and GIWAXS experiments revealed conclusively that CF$_3$-terminated molecular films dissolve irreversibly lose their long
range order during solvent vapor annealing, whereas CN-terminated molecules retain or improve their crystallinity while only softening without dissolution. The silyl groups played an important but secondary role as so far as the extent of which molecules with a given electron-withdrawing group was affected by the solvent vapor environment, with TCPS-substituted pentacene much less prone to vapor annealing than TIBS- and TIPS-substituted molecules.

In the last part, we investigated the solvent vapor annealing of TIPS-Pn and TIBS-CF₃-Pn films using different solvents and found the choice of solvent, and in particular its vapor pressure at room temperature to affect the extent of solvent uptake and determine whether the film remained rigid, softened, or dissolved.

**IV Solvent Vapor Annealing of Polymer-Molecule Blends**

In this chapter, we investigate the solvent vapor annealing of the P3HT donor polymer and P3HT:molecule (1:1 weight ratio) blends using all molecules investigated in the previous chapter in their pure form. Moreover, we investigate the solvent vapor annealing by toluene of P3HT:TIBS-CF₃-Pn blends with different blend ratios.
4.1 Solvent vapor annealing of P3HT thin films

In Fig. 4.1, we show QCM-D data [(a)-(c)], AFM images [(d), (e)] and optical micrographs [(f), (g)] of P3HT films subjected to toluene vapor annealing. As the solvent is introduced to the chamber, $\Delta F$ decreases and decays exponentially, indicating vapor uptake. Meanwhile, $\Delta D$ changes very little ($\Delta D < 2$), indicating almost no changes of the viscoelastic properties of the polymer even as significant mass of solvent is taken up. The rigidity of the polymer throughout the solvent vapor annealing process is rather surprising. Nevertheless, it lends itself well for Sauerbrey model analysis, the result of which (c) reveals the film to be taking in the equivalent of 50 nm layer of toluene liquid, with an initial rate of 0.39 nm/s.

Following the vapor annealing, the surface topography reveals fiberlike P3HT crystallites (e), while the aggregates observed before processing (d) become smaller or disappear all together. The RMS surface roughness decreased slightly from 1.41 nm to 1.32 nm after annealing process. From optical microscopy images [(f), (g)], it can be observed that large-scale aggregates become smaller.
Figure 4.1 The change of (a) ΔF, (b) ΔD and (c) thickness of P3HT film during solvent vapor annealing process. The [(d), (e)] AFM and [(f), (g)] optical microscopy images of the P3HT film (left) before and (right) after toluene vapor annealing.

4.2 Solvent vapor annealing of P3HT:TIPS-Pn and P3HT:PCBM blends

Just as we did in the previous chapter, we first investigate blends of P3HT with TIPS-Pn and PCBM. In Fig. 4.2, we find a very similar behavior as in the case of the pure molecules. Both blends take up a similar amount of solvent, nearly twice as much as the pure molecular films, while ΔD increases marginally for both cases. Interestingly, in the case of the P3HT:PCBM blend, ΔD increases more than either for pure P3HT or pure
PCBM. This suggests a composite effect may be at play as the significant solvent uptake by the blend changes the mechanical properties of the film.

Figure 4.2 The time-evolution of frequency [(a), (d)], dissipation [(b), (e)] changes and Saurbrey equivalent solvent thickness [(c), (f)] for P3HT:TIPS-Pn (left panels) and P3HT:PCBM (right panels) during toluene vapor annealing.

The initial rates of solvent uptake are 0.26 and 0.31 nm/s for P3HT:TIPS-Pn [Fig. 4.2(c)] and P3HT:PCBM [Fig. 4.2(f)], respectively. These rates of uptake are greater than the pure molecular films (0.1 nm/s and 0.27 nm/s for TIPS-Pn and PCBM, respectively), but lower than pure P3HT (0.39 nm/s), suggesting the rate of uptake is due to the solvent interacting with a composite material.
Figure 4.3 The [(a), (b)] AFM and [(c), (d)] optical microscopy images of the P3HT:TIPS- Pn film (left) before and (right) after solvent vapor annealing process.

The morphological changes of the P3HT:TIPS-Pn film before and after vapor annealing are shown from AFM images in Fig. 4.3 [(a), (c)]. Before annealing, the surface did not show any characteristic features, whereas the film subjected to annealing reveals some fine fiber formation as well as phase separation and, importantly, surface segregation of TIPS-Pn crystallites, which causes the RMS roughness to increase from 11.8 nm up to 13.2 nm. This is consistent with the dewetting and crystallization behavior observed for pure TIPS-Pn. It is also consistent with the observation of rising ΔD and slight splitting of ΔF overtones, which confirm that TIPS-Pn domains are softened and primed for mass transport. The significant roughening and phase separation indicate poor
blend characteristics for P3HT:TIPS-Pn, which would yield poorly performing OPV devices.

In case of the P3HT:PCBM blend, the morphological changes caused by solvent vapor annealing treatment are shown in AFM images presented in Fig. 4.4 (a) and (b), respectively. It can be seen that the topographically tall features subside, similar to the effect of toluene vapor annealing of pure P3HT, suggesting that these features are P3HT-related. The film roughness consequently decreases from 2.06 nm to 1.41 nm, indicating that the PCBM does not segregate to the surface. The blend film retains its integrity. Further device testing outside the scope of this thesis would be required to detect whether vapor annealing in these conditions improves device behavior or not. However, formation of P3HT fibers and dissolution of large surface asperities indicate the effects may be positive.

Figure 4.4. The AFM images of the P3HT: PCBM film (a) before and (b) after toluene vapor annealing process.
4.3 Solvent vapor annealing of P3HT blended with CF$_3$-terminated pentacene derivatives

The time-evolutions of \( \Delta F \) and \( \Delta D \) (Fig. 4.5) observed during solvent vapor annealing in blends with CF$_3$-terminated pentacene derivatives, namely P3HT:TIPS-CF$_3$-Pn (left panels), P3HT:TIBS-CF$_3$-Pn (center panels) and P3HT:TCPS-CF$_3$-Pn (right panels), are qualitatively similar to each other. They reflect a very different behavior than P3HT blends seen so far, *i.e.*, with TIPS-Pn and PCBM. There is significantly more vapor uptake and concomitant increase of \( \Delta D \), accompanied by significant splitting of \( \Delta F \) overtones, all of which suggest significant softening to the point of dissolution of the small-molecule acceptor domains inside the composite.

Figure 4.5 The [(a), (d), (g)] \( \Delta F \), [(b), (e), (h)] \( \Delta D \) and [(c), (f), (i)] thickness of the P3HT:TIPS-CF$_3$-Pn, P3HT:TIBS-CF$_3$-Pn and P3HT:TCPS-CF$_3$-Pn films during the toluene vapor annealing process.
A key characteristic of the blends is the fact that they take up substantially more solvent than the pure polymer. This may be due to the large internal interfacial area of the blend, to the ability of P3HT to swell without softening, and to the nanoscale size of small-molecule domains within the P3HT skeleton, which can act similar to a nanoporous material with large internal surface area and small pore radius, encouraging capillary effect.

The slight turnaround of $\Delta F$ in the case of P3HT:TIPS-CF$_3$-Pn suggests that the dissolved domains may not be supported by the surrounding P3HT matrix. In case of other molecules, the lack of a turnaround of $\Delta F$ and far less splitting of its overtones than in the case of the pure film suggest that the polymer acts as a supporting structure or scaffolding for the dissolving acceptor domains, where the pure molecular film would simply liquidify (see Fig. 3.3). The behavior of the blend, while strongly influenced by the supporting P3HT matrix, shows underlying influence of the silyl groups. For instance, P3HT:TCPS-CF$_3$-Pn soften the least, whereas P3HT:TIPS-CF$_3$-Pn softens the most and even dissolves partially. The behavior of P3HT:TIBS-CF$_3$-Pn is similar to that of P3HT:TIPS-CF$_3$-Pn blend.

From AFM data of the P3HT:TIPS-CF$_3$-Pn blend (Fig. 4.6) before (a) and after (c) the vapor annealing, we observe surface segregation of TIPS-CF$_3$-Pn from the blend, resulting in roughness increase from 7.51 nm to 12.1 nm. The optical micrographs also reveal significant coarsening after the vapor annealing process, consistent with
dissolution and reformation of the molecular domains, as observed from QCM-D. However, unlike in the case of pure molecular materials, the blended film completely wets the surface of the substrate, which is an important requirement for OPV devices.

Figure 4.6 The [(a), (c)] AFM and [(b), (d)] optical microscopy images of the P3HT: TIPS-CF$_3$-Pn film (left) before and (right) after toluene vapor annealing.

From Fig 4.7 (a) and (b), it can be observed that the morphologies of P3HT:TIBS-CF$_3$-Pn before and after solvent vapor annealing, respectively, are characterized by significant smoothing of the surface as RMS roughness decreases from 4.05 nm down to 2.64 nm. A similar observation is made in case of P3HT:TCPS-CF$_3$-Pn, for which we observe roughness decrease from 2.91 nm to 2.79 nm. TIPS-CF$_3$-Pn (as previously seen from TIPS-Pn) segregates to the surface of the polymer, whereas TIBS-CF$_3$-Pn and TCPS-CF$_3$-Pn do not appear to segregate to the surface.
Figure 4.7 AFM images of [(a),(b)] P3HT:TIBS-CF$_3$-Pn and [(c), (d)] P3HT:TCPS-CF$_3$-Pn films before (left) and after (right) toluene vapor annealing.

From these results, it appears that the P3HT plays a critical role in keeping the integrity of the polymer-molecule blend. It also appears that the silyl group plays an important role in determining whether the acceptor will remain blended with the donor or if it will segregate to the surface.

### 4.4 Solvent vapor annealing of P3HT blended with CN-terminated pentacene derivatives

In Fig. 4.8, we summarize the QCM-D results for toluene vapor annealing of P3HT:TIPS-CN-Pn and P3HT:TCPS-CN-Pn blends. As shown in Fig 4.8, $\Delta F$ decays exponentially in both cases, with slight splitting of the overtones of $\Delta F$. This indicates softening of the blends in region 2. $\Delta D$ increases moderately and much less so in case of
TCPS-CN-Pn than for TIPS-CN-Pn. This difference can be explained by recalling that the pure TCPS-CN-Pn film was the least soluble among all CF₃- and CN-terminated molecules. The initial rates of solvent vapor uptake are similar for both blends, yielding nearly double the rate of uptake of the pure molecular films, but still less so than the pure polymer film.

Figure 4.8 The [(a), (d)] ΔF, [(b), (e)] ΔD and [(c),(f)] thickness changes of the P3HT: TIPS-CN-Pn and P3HT: TCPS-CN-Pn film during toluene vapor annealing.

In Fig. 4.9 [(d), (e)] we show AFM images of the P3HT:TIPS-CN-Pn blend before and after solvent vapor annealing, respectively. The images reveal rough surfaces in both cases increasing from 12.3nm to 23.2nm. Significant coarsening follows the vapor
annealing process. The surface features resemble far less the typical P3HT fibers than molecular crystallites segregated at the surface.

Figure 4.9 The AFM images of the P3HT: TIPS-CN-Pn film (a) before and (b) after toluene vapor annealing.

By contrast, the P3HT:TCPS-CN-Pn blend appears to be much smoother and finer in Figs. 4.10 (a) and (b). Here, vapor annealing causes surface asperities to disappear, resulting in very fine blend morphology suitable for organic solar cells. The surface roughness changes from 2.06 nm to 4.79 nm after vapor annealing.

Figure 4.10 The AFM images of the P3HT: TCPS-CN-Pn film (a) before and (b) after toluene vapor annealing.
4.5 Influence of functional groups

Comparison of the AFM results for the various blends reveals that surface segregation occurs only in the case of TIPS-substituted molecules. This cannot be explained by solubility of TIPS-substituted molecules in toluene, because TIPS-Pn shows the least solubility of all pentacene derivatives investigated in this thesis. The behavior is consistent even when a CF$_3$ group is present, suggesting that TIPS-substituted acceptors are not compatible with P3HT donor and thermodynamic driving forces favor separation of the acceptor from the blend. By contrast, TIBS- and TCPS-substituted molecules form a more intimate blend and the blend surface becomes smoother after toluene vapor annealing, proving the compatibility of the donor and the acceptor.

To compare the behavior of the composite blend to the pure molecular films, we summarize in Fig. 4.11 the initial rates of solvent vapor uptake all films (blends and pure materials) investigated as part of this thesis project.

Comparing the blends with pure molecules baring the same electron withdrawing groups, we find that CF$_3$-terminated materials consistently show the fastest vapor uptakes.

We find consistently higher rates of uptake by the polymer:molecule blends than by the pure material. This is partly due to the fact that the blends are significantly thicker than the pure materials, as the starting solutions of the pure and blend films were 10 mg/ml and 20 mg/ml, respectively. However, this does not explain fully what is the process initiated by adsorption on surfaces. For instance, the case of P3HT:PCBM, which
exhibits a rate of solvent vapor uptake that is slightly larger than the pure PCBM and slightly less than the pure P3HT film, despite being prepared from a 20 mg/ml solution. Comparing this to TIPS-Pn, we find that the rate of uptake of the blend is more than double the pure molecule, but still lower than pure P3HT. A similar behavior is also noted in the case of CN-terminated molecules, where all rates of uptake all lower than that of the pure P3HT. In the case of CF$_3$-terminated molecules, we observe that the blend has a higher rate of uptake than pure P3HT, even in the case of TCPS-CF$_3$-Pn, which in pure form also has a slower rate of uptake than P3HT.

![Figure 4.11 Comparison of vapor uptake rates by P3HT, P3HT: molecule blends and respective pure molecules.](image)

These results suggest that the solubility of the acceptor plays an important role in the ability of the D-A blend to take up the solvent. In addition, the morphology of the blend,
characterized by a large D-A interfacial area, and nanoscale domains with very large radii of curvature can draw solvent into the blend via capillary forces.

4.6 Solvent vapor annealing on different donor-acceptor blend ratio

The structural integrity of blends where one component can fully dissolve is important to consider. As shown above, dissolution of the acceptor does not imply its segregation and separation from the blend (e.g., TIBS-CF$_3$-Pn and TCPS-CF$_3$-Pn), unless there are thermodynamic reasons. This appears to be the case of TIPS-substituted pentacene, which consistently separated from the blend. To further understand the contributions of the polymer to supporting and binding during solvent vapor annealing, we investigate the vapor annealing of P3HT:TIBS-CF$_3$-Pn blends with different polymer:molecule blend (by weight) ratios. The blend ratios (P3HT: TIBS-CF$_3$-Pn) were selected as 4:1, 1:1, 1:4, 1:9, and 1:19.

In Fig 4.12 [(a)-(c)] we plot the changes of the third overtones of $\Delta F$ and $\Delta D$, as well as the equivalent Sauerbrey thickness change for the different ratios. At high polymer content (4:1), $\Delta D$ remains near zero during the first 100 s of the annealing process even as $\Delta F$ shows evidence of significant uptake. With increasing acceptor loading, we find the onset of $\Delta D$ variation shifts to earlier time, the slope of $\Delta D$ increases dramatically, and the maximum $\Delta D$ reached during vapor annealing increases as well. Meanwhile, $\Delta F$ undergoes a turnaround for blend ratios greater than 1:4, i.e., 1:9 and 1:19, which behave
much like the pure molecular film in that they dissolve and liquefy. From these observations, it would appear that the polymer binds the blend together even for ratios of 1:4 (polymer:molecule). Blends with ratio of 1:9 and higher behave more like a pure molecular film as so far as the mechanical properties of the blend.

![Figure 4.12 The (a) ΔF, (b) ΔD and (c) thickness change of the P3HT: TIBS-CF3-Pn blend with the ratio of 4:1, 1:1, 1:4, 1:9 and 1:19 in solvent vapor annealing process.](image)

In Figure 4.13, we plot the initial rates of uptake of pure TIBS-CF3-Pn, P3HT and blends thereof. The rate of uptake up to 1:1 weight ratios of P3HT and P3HT:TIBS-CF3-Pn are higher than the pure polymer, but less than the pure acceptor.
However, all acceptor-rich blends appear to show significantly higher rates of uptake than either the pure polymer or the molecular film, which suggests the morphology and phase separation are quite different than the pure molecular film. The highest rate of 2.9 nm/s is seen in case of 1:4 blend.

Figure 4.13 Comparison of the initial rates of vapor uptake during toluene vapor annealing of TIBS-CF$_3$-Pn, P3HT and P3HT:TIBS-CF$_3$-Pn blends with different weight ratios.

AFM images of the blend surface and the associated RMS surface roughness values before and after toluene vapor annealing are shown in Fig. 4.14 and Table 4.1, respectively. The morphologies of the 4:1 and 1:1 blends are very similar to each other and to pure P3HT (both before and after annealing). In both cases, vapor annealing reduces the surface roughness of the blend, indicating more intimate mixing of the donor and the acceptor. All other blends appear to show the surface is coated with a thin layer of excess molecular crystallites that are highly oriented in the plane of the substrate. These surface features disappear after solvent vapor annealing and are replaced with a fiber-like
surface morphology, indicating increased mixing with the polymer, which results in roughening and coarsening of the surface. In cases of excess molecular material in the solution, smooth and long crystallites are on top of the polymer, because the latter deposits first as it is less soluble than the molecules. It is worth noticing that vapor annealing does not cause dewetting in any of the samples – in contrast to the pure molecular film.

The behavior of blends very much depends on the vapor interaction with the acceptor molecules, with the electron withdrawing group playing a major role in determining the rate of solvent uptake and the extent of softening or dissolution. Nevertheless, even the blends of P3HT with (TIPS, TIBS, TCPS)-CF3-Pn became softened rather than fully dissolved, suggesting an important role of the polymer matrix.

Table 4.1 Summary for the roughness changes of P3HT, P3HT:TIBS-CF3-Pn blends with ratios of 4:1, 1:1, 1:4, 1:9 and 1:19, and TIBS-CF3-Pn pure molecule before and after toluene vapor annealing.

<table>
<thead>
<tr>
<th></th>
<th>P3HT</th>
<th>4:1</th>
<th>1:1</th>
<th>1:4</th>
<th>1:9</th>
<th>1:19</th>
<th>TIBS-CF3-Pn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughness before annealing (nm)</td>
<td>1.41</td>
<td>4.47</td>
<td>4.05</td>
<td>2.09</td>
<td>0.89</td>
<td>1.18</td>
<td>4.95</td>
</tr>
<tr>
<td>Roughness after annealing (nm)</td>
<td>1.32</td>
<td>1.94</td>
<td>2.64</td>
<td>4.83</td>
<td>4.01</td>
<td>2.62</td>
<td>33.5</td>
</tr>
</tbody>
</table>
Figure 4.14 Changes in surface morphology of P3HT:TIBS-CF₃-Pn blends prepared with [(a), (b)] 4:1, [(c), (d)] 1:1, [(e), (f)] 1:4, [(g), (h)] 1:9, and [(i), (j)] 1:19 blend ratios before and after toluene vapor annealing, as measured by AFM.

4.7 Conclusion

In this chapter, we investigated the toluene vapor annealing of bulk heterojunctions based on P3HT and a variety of acceptor molecules, including PCBM, TIPS-Pn, and other
pentacene derivatives. We found that the P3HT polymer behaves as a matrix and support structure to the acceptor, even as it softens or dissolves and liquefies.

The role of the silyl group emerged here as more important than in the previous chapter, as it determined the final outcome of the blend in terms of segregation to the surface. The morphologies of the blends are also dominated by silyl groups and moderated by the presence of P3HT. In case of TIPS-substituted pentacenes, the molecules consistently separated from the blend and deposited on the surface as crystallites. This behavior was not observed for neither TIBS- or TCPS-substituted molecules, even when they showed evidence of significant softening and dissolution, as in the case of TIBS-CF₃-Pn. It suggests that thermodynamic driving forces do not favor blending of TIPS-substituted pentacene derivatives with P3HT, making it less suitable for OPV applications.

When comparing the influence of solvent vapor annealing on blends with different ratios of P3HT:TIBS-CF₃-Pn, we find the behavior resembles that of the polymer when the blend is loaded with P3HT, and more TIBS-CF₃-Pn-dominated in the presence of excess acceptor. As-deposited films with excess acceptor loading were found to be covered with acceptor crystallites. Subsequent toluene vapor annealing led to increased mixing of the blend.
The rates of solvent vapor uptake in blends containing excess acceptor were greater than those of either pure polymer or pure molecule, suggesting that vapor uptake and annealing are influenced by the phase separation and morphology of the blend.
V Conclusion

In this thesis, we demonstrated *in situ* QCM-D and *in situ* GIWAXS as a powerful set of techniques to monitor *in situ* and in real time the solvent vapor uptake and resulting effects on thin film structural and viscoelastic properties. *In situ* GIWAXS was particularly useful to identify optimal vapor annealing conditions (e.g., for TIPS-Pn), and to reveal which functional groups cause materials to dissolve and which ones prevent materials from recovering their crystallinity after vapor annealing. QCM-D was also very insightful when investigating the vapor annealing behavior of polymer-molecule blends. This insight is very useful for developing effective and well-tailored post-production processing strategies, as well as for designing molecular building blocks which are high performing and compatible with vapor annealing.

We compared the toluene vapor annealing of two well-known materials, namely TIPS-Pn and PCBM, and their blends with P3HT. We found that the P3HT polymer behaves as a matrix and support structure to the acceptor, even as it softens or dissolves and liquefies. TIPS-Pn film softens when exposed to toluene vapor, while PCBM does not. An optimal vapor annealing window of 100s exists for TIPS-Pn, during which the crystallinity improves. This is followed by a period of decreased crystallinity and softening, during which significant molecular reorganization, mass transport and dewetting modify the thin film into isolated crystallites.
We also investigated and compared solvent vapor annealing behaviors of pentacene derivatives terminated with different electron withdrawing groups, namely CF$_3$ and CN, and different solubilizing silyl groups, namely TIPS, TIBS, and TCPS. QCM-D analysis reveals conclusively that the electron-withdrawing groups are much more consequential than silyl groups in determining the fate of molecules during solvent vapor annealing. The combination of QCM-D and GIWAXS experiments revealed conclusively that CF$_3$-terminated molecular films dissolve irreversibly lose their long range order during solvent vapor annealing, whereas CN-terminated molecules retain or improve their crystallinity while only softening without dissolution. The silyl groups played an important but secondary role as so far as the extent of which molecules with a given electron-withdrawing group was affected by the solvent vapor environment, with TCPS-substituted pentacene much less prone to vapor annealing than TIBS- and TIPS-substituted molecules.

The behavior of blends very much depends on the vapor interaction with the acceptor molecules, with the electron withdrawing group playing a major role in determining the rate of solvent uptake and the extent of softening or dissolution. Nevertheless, even the blends of P3HT with (TIPS, TIBS, TCPS)-CF$_3$-Pn became softened rather than fully dissolved, suggesting an important role of the polymer matrix.

The role of the silyl group emerged in blends as more important than in pure acceptors, as it determined the final outcome of the blend in terms of segregation to the surface. The
morphologies of the blends are also dominated by silyl groups and moderated by the presence of P3HT. In case of TIPS-substituted pentacenes, the molecules consistently separated from the blend and deposited on the surface as crystallites. This behavior was not observed for neither TIBS- or TCPS-substituted molecules, even when they showed evidence of significant softening and dissolution, as in the case of TIBS-CF₃-Pn. It suggests that thermodynamic driving forces do not favor blending of TIPS-substituted pentacene derivatives with P3HT, making it less suitable for OPV applications.

When comparing the influence of solvent vapor annealing on blends with different ratios of P3HT:TIBS-CF₃-Pn, we find the behavior resembles that of the polymer when the blend is loaded with P3HT, and more TIBS-CF₃-Pn-dominated in the presence of excess acceptor. As-deposited films with excess acceptor loading were found to be covered with acceptor crystallites. Subsequent toluene vapor annealing led to increased mixing of the blend.
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