INTERFACE STUDIES OF SMALL-MOLECULE ORGANIC PHOTOVOLTAICS:
SURFACE MODIFICATIONS, ELECTRON DONOR TEXTURING, AND CO-FACIAL
VARIATIONS AT THE DONOR/ACCEPTOR HETEROJUNCTION

By
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DEDICATION

I dedicate this to my mother, Luisa Placencia…a single mother of three kids who raised us under insurmountable odds…this one’s for you ma.
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ABSTRACT

The role of the oxide/organic and organic/organic interfaces in small-molecule planar-Heterojunction (PHJ) photovoltaics was investigated with three interrelated projects: i) indium-tin oxide (ITO) bottom contact electrodes were modified with gold nanoparticles (Au-NPs) to improve rates of charge-transfer at the donor/oxide interface, ii) donor layers in OPVs were textured to increase charge generation at the organic/organic interface, and iii) the effect of co-facial overlap on device performance via tuning of the electron acceptor orientation at the organic/organic interface. The modification of ITO with Au-NPs showed increased performance in small-molecule OPVs when compared to non-processed ITO devices due to the interactions between the Au-NPs and the donor material. Textured TiOPc increased overall device performance by a factor of 2X via the increased surface area, near-IR absorption, and increased mobilities. Modified and un-modified PTCDA acceptors showed that co-facial overlap at the organic/organic interface is a large determinant in device performance, while the performance in small-molecule planar-heterojunction photovoltaics were severely affected by the pre-treatment process, most likely due to the particular interactions between the oxide and the donor material.
CHAPTER 1: INTRODUCTION

1.1 The Case for Solar

As the world leader in technology development and energy consumption, the United Stated of America is poised to highly diversify its energy portfolio. This diversification will allow for an amount of economic insulation from dramatic commodities price swings and most importantly, partially divorce national security from hostile states that posses the resources needed to maintain the status quo. To date, this situation has yet to be realized. According to the Energy Information Administration, 84 % of the total energy consumption within the United States comes from non-renewable sources (i.e. coal, petroleum, etc.). Figure 1.1 shows a breakdown of U.S. energy consumption as of FY 2008.¹

From this information, it can be seen that renewable sources only makeup 7% of the energy portfolio. Due to the abundance of “energy corridors” within the U.S. landmass (e.g. wind in the Texas panhandle area, solar in the southwest), exploitation of these resources is currently limited only by A) the capital-intensive investments required to build new power facilities and/or B) underdeveloped technology. With the latter seen as the only option viable for true progress in energy diversification, the need for intense research and funding into these technologies has only heightened. One of the most promising renewable technologies, with substantial investments and heavy R&D already underway, is solar photovoltaic technology.
Photovoltaic Systems: Quick Overview

Photovoltaic devices are classified as either Inorganic or Organic, with corresponding subsections under each. Inorganic photovoltaics are composed of Metals, Metalloids, and Non-metals, with the latter used as dopants within some systems. Organic photovoltaics are comprised mainly of non-metals, with carbon-based structures being the most abundant within such systems. While the elemental makeup between the two systems is notable, the largest difference derives from the mechanistic portions of the current generating process. Figure 1.2 gives an overview of the operational mechanism for the two classes of technologies, where small-molecule planar-heterojunction technology was chosen to represent organic PV systems.
Wherein the absorption process and collection of charges are relatively comparable, the differences are seen in the type of excited state that is generated and the charge-separation process. In inorganic PVs, the dielectric constant of the material allows for the charge separation to occur just by the absorption process, where free charge-carriers are generated instantly. In organic PVs, the low dielectric constant results in a type of excited state that requires interface energy mismatches to generate the dissociation of the charge-carriers. Aside from carrier generation, the differences in the excited state limits the thicknesses which can be used for organic systems which is typically on the order of 300 nm at the very most, in contrast to micron thicknesses for inorganic systems. This in turn leads to low light absorption and hence, lowers overall efficiency of the system.

Figure 1.2: Inset (A) shows the typical process for photocurrent generation in inorganic photovoltaic devices. Inset (B) shows the operational mechanism of organic photovoltaic systems. The biggest differences between the two systems derive from their exciton dissociating abilities, where the inorganic dissociates via the absorption process, where organic require an energy offset for dissociation.
1.3 Inorganic Photovoltaic Technology: Silicon Technology

As one of the most efficient and commercially viable technologies on the market, monocrystraline PVs have reached modules efficiencies of 22.9%. Development of this technology has been underway for many years, with the first commercial modules being offered by SHARP Corp. in 1963. Since then, significant efficiency milestones have been reached, with major contributions coming from Green and co-workers at UNSW. State of the art monocrystraline PVs consist of a single junction with aluminum and silver as bottom and top contacts (Figure 1.3). The single silicon junction consists of a p-doped and n-doped region with an overall thickness of 200 microns.

![Figure 1.3: Cross sections [Inset (A)] and image of a cell [Inset (B)] of a monocrystraline silicon solar cell.](image)

In order to account for reflection losses and absorption deficiencies (due to silicon’s indirect bandgap), anti-reflection coatings (A/R coating) and roughening of the silicon surface is a common manufacturing process. The properties that make monocrystraline silicon suitable for PV applications are numerous, the most important of them being purity. Impurities for Semiconductor Grade Silicon (SG-Si or 99.999999% pure) are located near the low (1>) parts per billion (ppb). Due to the high purity of the material,
electron and hole mobilities are significantly higher than any material in the marketplace used for photovoltaic applications (ue = ~1300 and uh = ~480 cm²/V*s).³ Aside from purity-related advantages, the absorption profile of silicon also contributes to performance. Absorption by silicon within the visible portion of the electromagnetic spectrum is ideal due to the high photon flux that is observed in the AM 1.5 G spectral profile in between 600 and 800 nm (see Chapter 2).

Despite the advantages possessed by silicon photovoltaic technologies, and other inorganic systems not discussed here, cost per unit watt-peak (Wₚ) continues to be relatively high. The drive to further reduce this ratio to the Department of Energy’s mandate of $1/Wₚ without subsidies for carbon-free energy has led to attention being placed on thin-film and other alternative technologies. Focusing on organic semiconducting materials, we turn our attention towards this segment of photovoltaics.

1.4 Organic-Based Photovoltaic Technology

Photovoltaic technologies based on organic semiconductors are still some years away from making significant impact upon the marketplace due to their relatively low efficiencies (ca. 8%) for research grade systems.⁶ However, the potential to develop low-cost portable power has led companies such as Konarka, Solamer, Dye Sol, and Heliatek to invest heavily into technology development. This, coupled with an intense research effort by academia, is certain to make this technology succeed in the long term.

Organic photovoltaic technology is comprised of several subunits of technology which are: 1) small-molecule planar heterojunction (PHJ) technology, 2) polymer-based
bulk-heterojunction, and alternatives like 3) dye-sensitized and 4) hybrid technologies. Small-molecule technology uses low molecular weight systems that are vacuum deposited one active layer at a time. Bulk-heterojunction systems are solvent blends of donor/acceptor polymers that are spin-cast followed by deposition of an inorganic salt and metal top contact. Dye-sensitized technologies make use of a metal oxide, usually titanium dioxide, along with an adsorbed dye on the oxide, electrolyte, and redox couple. Hybrid technologies make use of inorganic systems as either donors or acceptors in an effort to exploit their intrinsic abilities to collect and dispose of charge readily. In the following, a review of the history, technology and the mechanistic processes in organic photovoltaics is presented.

1.4.1 Basics of Organic Semiconductors and Their Processes in Photovoltaics

1.4.1.1 Structural Aspects

Organic semiconductors are almost always created from conjugated aromatic hydrocarbons. The location of this conjugation relative to functional groups, metal centers, and/or other identical sub-units (e.g. oligomers) can lead to changes in spectral response, packing density, or charge transport properties. One example of a change in structural properties as a function of metallated center is the phthalocyanine molecule (Figure 1.4).

Resembling the heme unit found in red blood cells, this conjugated semiconductor has the ability to coordinate many metals, resulting in the tunability of its molecular properties (e.g. optical, electrical). Copper phthalocyanine (CuPc) is the most widely
used semiconductor in the organic electronics research field, where it has found use in photovoltaics,\textsuperscript{8,9} OFETs,\textsuperscript{10,11} and many other applications.\textsuperscript{12,13} CuPc has been shown to orient itself parallel to surfaces such as HOPG and single crystal silver in the first few layers.\textsuperscript{14,15} Structurally shown to be planar, the molecule arranges itself into different polymorphs, changing edge-angles between adjacent molecules (Figure 1.5).\textsuperscript{16} Changing the metal center to a tri or tetravalent species alters the structural confirmation. These systems assume a puckered geometry in which the metal center sticks out of the parallel plane of the phthalocyanine ring, resulting in relatively strong internal dipoles.\textsuperscript{17,18} In a solid crystal structure, they orient themselves in a head-to-head and tail-to-tail arrangement, described as \textit{concave} and \textit{convex} pairs. These molecular arrangements affect the photoconductivity of these systems dramatically, therefore altering their device

Figure 1.4: Un-metallated phthalocyanine, also known as H$_2$Pc [Inset (A)], and the iron protoporphyrin IX in hemoglobin, which is the oxygen-transport metalloprotein in red blood cells. The phthalocyanine base unit can be metallated with a large host of metal ions to give varying properties with respect to absorption and electron transport.
performance. In addition to these slight structural differences, peripheral modifications of these semiconductors can likewise lead to changes in device performance.

### 1.4.1.2 Interactions with Light

Any organic semiconductors being evaluated for PV applications must have optical transitions that occur in the visible/near-IR portion of the electromagnetic spectrum. The simplified process of light interaction with these organic semiconductors begins with the absorption of the energy, resulting in a HOMO-LUMO $\pi$ to $\pi^*$ transition. A typical UV/Vis absorption spectrum for titanyl phthalocyanine (TiOPc) is shown in Figure 1.6. The absorption spectrum shows little activity above the 1000 nm onset. This onset represents the lowest energy optical transition allowed within the system and can be used to determine the optical bandgap.

![Figure 1.5: Structural arrangements of some of the polymorphs of copper phthalocyanine [Inset (A) and (B)] and tri and tetravalent phthalocyanines. A change of the metal center is a major contributor to the arrangement taken up by the entire unit in the bulk structure. While copper phthalocyanine arranges in ordered disks or herring bone structures, the tri and tetravalent phthalocyanines typically arrange in a head-to-tail fashion.](image-url)
1.4.1.3 Transport Gaps, Optical Gaps, and Charge Transport

The dielectric constants of organic semiconductors are small relative to inorganic systems such as barium titanate and other perovskites.\textsuperscript{20,22} This derives from the inability of covalent bonds to delocalize charge across large distances (40 – 100 Å) during excited state processes. When excited states exist, as coulombically bound electron-hole pairs, they are termed excitons; the properties of which are classified according to their delocalization properties. Unlike \textit{Wannier-Mott} excitons or just \textit{Wannier} excitons, which can delocalize across large molecular distances, excitons in organic semiconductors can only delocalize across \( \sim 5\text{Å} \).\textsuperscript{19} These types of excitons are referred to as \textit{Frenkel}, and are usually localized within a single molecule. The other type of common exciton in organic systems is the \textit{Charge-Transfer} (CT) exciton, where the exciton is delocalized across two molecular units (Figure 1.7). In addition to small localization distances, there are also differences in the lengths over which these excitons can diffuse prior to recombining.
Inorganic materials have long diffusion lengths, on the order of microns, while organic materials have very small exciton diffusion lengths (10 – 20 nm).

Organic semiconductors have two gaps associated with them; the *Transport* gap and the *Optical* gap. The creation of either a Frenkel or CT exciton results from optical transitions, which do not lead to free charge carriers. There is usually an additional amount of energy required in order to generate free charge carriers, which is a consequence of the electrostatic interactions between the hole and electron. This energy can be as high as 1 eV for some systems.\(^{20}\) The dissociation energy of the exciton cannot be directly determined via optical spectroscopy. Inverse photoemission spectroscopy (IPES), in combination with UV photoelectron spectroscopy (UPS), are the methods of choice for determining transport gaps and the energy required for dissociation.\(^{20}\) Inorganic semiconductors are the opposite of organic semiconductors, where the optical

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**Figure 1.7**: Lattice structure showing the different types of excitons that can be generated in all materials. [Reproduced from reference \(^{19}\)]
and transport gaps can be assumed to be the same due to the ability of the exciton to freely dissociate as a result of the low binding energy characteristics of Wannier excitons.

Charge transport in organic semiconductors is different than that seen in inorganic systems. This is a result of the closely spaced energy levels in inorganic systems that lead the formation of energy bands. These bands can be thought of as continuous energy levels in which charges can be made to transport laterally from atom to atom. Organic systems do not have such continuity in energy levels due to the small overlap in wavefunctions between individual molecules, leading to smaller bandwidths than those seen in inorganic systems. This results in charge transport via a hopping and/or tunneling mechanism.\textsuperscript{19,23}

During the excitation process in organic solar cells, the exciton diffuses under the influence of a concentration gradient, due to either its recombination or dissociation at the interface. This process resembles that seen in \textit{Le Chatelier's Principle}, where excitons randomly move towards the interface due to their absence. Once at the interface, the transfer of the electron to the acceptor occurs, though the hole and electron are still bound to each other, which is denoted as the \textit{polaron pair}. Giebink and co-workers have recently developed a theory for the operation of solar cells based on the concept of polaron pairs.\textsuperscript{24,25} Based on their idea, the excess energy that is required to freely dissociate the quasi particle into free polarons is one of the many reasons for the decreased performance on OPVs. After dissociation, the polarons migrate towards the corresponding electrodes under the influence of an electric field and collected. During this process, many factors such as crystallinity, mobility, and active layer thickness affect
the device performance. One of the most critical, however, is the numerous interfaces between critical layers within the device.

1.4.2 Organic Semiconductor Interfaces in OPV Devices

1.4.2.1 Organic/Oxide Interface

Characterization of organic/oxide interfaces has only recently begun to be of interest due to the observed effects whenever the energetics of these interfaces is altered with pre-treatments such as polymer buffer layers or plasma etching processes. In addition to the ITO/organic heterojunction, interest in the interface between organics and metal oxide hole extracting layers has also increased. As shown by Irwin and co-workers, the inclusion of a nickel oxide interlayer increased the performance of polymer solar cells via improvements in the fill factor and open-circuit photovoltage. Others like Shrotriya et al. demonstrated improvements using other transition metal oxides, but with poorer performance as that shown by Irwin. Still, the interest in these interlayers continues to grow, with the realization that understanding the energetics of the interface will be the only way to ultimately increase device performance beyond the current record of 8%.

Recognizing the importance of these interfaces, Jones and Smith have worked together to understand the interface between small molecules and ITO, along with small molecules and metal oxide interlayers. Their work on the modification of CuPc/C₆₀ devices with molybdenum oxide interlayers (MoO₃) is a good example. Using vacuum deposition techniques, Jones et al. showed that deposition of 5 nm of MoO₃ on ITO improved the open-circuit photopotential and fill factor for some systems (Cl-AlPc,
SubPc) while decreasing the performance in others. They attributed the increase in overall performance to better alignment of the HOMO of the donor systems to the mid-gap states of the molybdenum oxide allowing for a more efficient hole-extraction process. Smith et al. went on to study the effect of modifying ITO with MoO$_3$ and the effect on the MOx/CuPc interface. The presence of a significantly higher work function was hypothesized to increase the built-in field within the system, further increasing the ability to enhance the open-circuit photopotential. These works highlight the importance of understanding the oxide/organic interface, showing that molecular level approaches can give insight into macroscopic device behavior.

1.4.2.2 Organic/Organic' Interface

Organic-organic heterojunctions in OPVs have gathered much attention recently due to their role in determining device operation. As discussed previously, the process for charge generation in an OPV consists of several steps, of which the charge-separating step pertains exclusively to organic/organic interfaces. In addition, it has been qualitatively shown that the open-circuit photopotential is strongly influenced by the $E^D_{\text{HOMO}} - E^A_{\text{LUMO}}$ difference. The first effort which attempted to quantitatively describe the effects of the relationship between interface energetics and device operation was published by Potscavage and co-workers.$^{34}$ In this work, a series of donor molecules that varied in their first ionization potential (HOMO) were singularly paired with C$_{60}$ in a planar-heterojunction architecture. The differences in dark current densities, along with the temperature dependent response of the pentacene/C$_{60}$ cells under no illumination were
recorded. The central hypothesis of the authors focused on the origin of the open-circuit photovoltage and the relationship to the dark current density. The researchers argued that a large portion of the dark current density derived from a Boltzmann-like temperature dependent barrier, which could be substituted into the dark current density, which is connected to the open-circuit photopotential via (1.1):

\[
V_{OC} \approx \frac{n kT}{e} \ln \left( \frac{J_{SC}}{J_0} \right) \quad (1.1)
\]

where \( J_{SC} \) is the photocurrent density, \( J_0 \) the dark current density, \( n \) the ideality factor, \( kT \) the thermal energy, and \( e \) the elementary charge.

Further experiments focused on understanding this effect and its implications on device performance came from Perez and co-workers.\(^{35} \) Their work also explored the origins of the open-circuit photopotential, with specific focus on its relation to the structure of the donor and the implications on interface energetics. They synthesized a series of structurally unique electron donating molecules and correlated co-facial contact between the donor and acceptor based on crystallinity measurements using x-ray diffraction (XRD). Their results showed that with greater co-facial contact within the donor, comes a greater amount of photogeneration with a consequent decrease in photovoltage. They assumed that similar results would be seen if acceptors with varying degrees of crystallinity were used. These results then led to the modification of the open-circuit photopotential equation which was proposed by Potscavage et al. (1.1) to the newly modified version (1.2), based on fits of their data:

\[
V_{OC} = \frac{n kT}{q} \ln \left( \frac{J_{SC}}{J_{SO}} \right) + \frac{\Delta E_{DA}}{2q} \quad (1.2)
\]
Where $J_{SO}$ is the prefactor determined experimentally, $n$ the ideality factor, $kT$ the thermal energy, and $\Delta E_{DA}$ the effective barrier. The effective barrier is calculated from the difference between the HOMO of the donor and the LUMO of the acceptor.

Giebink and co-workers have gone a step further by trying to analytically quantify the processes that affect photocurrent generation and the open-circuit photopotential.$^{24,25}$ Using a polaron pair generation and recombination model, they were able to reproduce the device behavior of CuPc and SubPc, while claiming to also predict the behavior of polymer photovoltaics. From their analytical expression, several key parameters such as the dark current, short-circuit current density, and the open-circuit photopotential were predicted. The work showed that the organic/organic’ interface plays a crucial role in the operation of the device, where molecular-level aspects of device processing ultimately determine performance parameters. The models that have been developed used planar-heterojunction architectures because of the exquisite control in building these interfaces. Although further work is needed in demonstrating the universal nature of these analytical expressions, they still represent an important starting point for developing an understanding of the organic/organic’ interface in OPVs.

1.4.2.3 Organic/Metal Interfaces

The other interface that is of importance in the study of organic photovoltaics is the organic/metal heterojunction. Several groups have investigated this interface in the context of OPV devices. Kahn and co-workers have undertaken a series of studies on the complicated nature of this interface using photoemission spectroscopy and device
characterization.\textsuperscript{36} Their results show that many factors such as deposition temperature, experimental layout, and processing all affect device performance.

The processing of small-molecule photovoltaics rely on the deposition of a buffer layer between the acceptor and the metal contact (usually a low work function species like aluminum or magnesium). The most commonly used buffer systems are bathocuproine (BCP)\textsuperscript{37} and Tris-(8-hydroxyquinone) (Alq3),\textsuperscript{38} whose structure are shown in Figure 1.8.

![Figure 1.8: Kekule and molecular simulations of the most common metal/acceptor selective interlayers used in OPVs.](image)

These small-molecule systems have been shown to increase device performance, and as shown by Forrest et al., have been shown to form very complex interfaces.\textsuperscript{39} Gommans et al. investigated the role of BCP in SubPC/C\textsubscript{60} devices (and in devices without the donor) to study the effect on the built-in potential.\textsuperscript{37} Their results showed that BCP helps
to prevent the creation of donor states between C_{60} and aluminum. Furthermore, an increase in the built-in potential was noted, which helps to increase the open-circuit photopotential. The work by Davis et al. was also motivated by the effects that these buffer layers have on organic electronics.\textsuperscript{38} Surface Raman spectroscopy was used to probe the active bonding modes between the metal and the buffer layer. Their results show that major changes in the spectral lines take place between 5 and 20 angstroms. During the deposition of the first couple of monolayers, graphitic carbon was found to develop. This was suspected to lower the amount of energy required for electron transfer, hence justifying the improvements seen with the inclusion of Alq3 in OLED and OPV systems.

The works discussed within this section have shown that interfaces play a large role in device operation. The properties of the materials used are only one factor that should be considered when optimizing emerging OPV systems. The complex natures of these interfaces show that without a thorough understanding of the interface science, progress within the field is likely to be slow at best.

1.4.3 Generation III Photovoltaic Systems

1.4.3.1 Small-Molecule Planar-Heterojunction PVs

The first planar heterojunction PV device was created by C.W. Tang at \textit{Eastman Kodak Company} in 1986.\textsuperscript{40} In this work, Tang realized that single layer OPVs could not be made to achieve higher performance due to the inability to separate enough charges with respect to the recombination process.\textsuperscript{41} His use of copper phthalocyanine (CuPc) as
the electron donor and a perylene tetracarboxylic derivative as the electron acceptor allowed for a maximum efficiency of 1% under air:mass 2 (AM 2) illumination. After Tang’s early success, an entirely new field in the science & technology of small-molecule photovoltaics was created that resulted in significant enhancements over his original concept. These advances have come as a result of increasing the surface contact area between the donor and acceptor, the use of new acceptors with higher charge mobilities, and exploration into new architectures for maximum spectral absorbance.

Small-molecule planar heterojunction systems make use of two organic semiconductors whose charge-carrying properties resemble that of p-type and n-type semiconductors. They are vacuum deposited sequentially, leading to an interfacial energy offset making exciton dissociation possible. **Figure 1.9** is a schematic of a research-grade planar-heterojunction OPV with the donor, acceptor, and buffer interlayer used for the research presented in this dissertation. To a first approximation, offset energies between

![Figure 1.9: Cross-section of a small-molecule planar-heterojunction OPV device, along with the molecular structures of each molecule. This system is the main basis for the series of studies that are described in the chapter below.](image)
the occupied and unoccupied levels of the donor and acceptor can be used to predict device performance.\textsuperscript{24,25}

![Diagram of molecular structures](image)

Figure 1.10: Cross-section of a small-molecule planar-heterojunction OPV device, along with the molecular structures of each molecule. This system is the main basis for the series of studies that are described in the chapter below.

The energy difference between the LUMO of the donor and the LUMO of the acceptor is proportional the photocurrent density; the offsets between the HOMO of the donor and the LUMO of the acceptor is proportional to the open-circuit photopotential of the device (Figure 1.10). In choosing molecular semiconductors to make functioning devices, offset energies must not provide too much of a difference or too little, for if one parameter is optimized, the other will be compromised in the process.\textsuperscript{21,23} For example, if the goal is to maximize the open-circuit photopotential, the $E_{\text{LUMO}}^D - E_{\text{LUMO}}^A$ difference must decrease, therefore affecting the amount of photocurrent that is generated. Rand and
co-workers have written a good review which provides a much more rigorous consideration of the offset energies in small-molecule OPVs.\textsuperscript{42}

Advances in the field of small-molecule planar-heterojunction photovoltaics have been made in 1) creating nanostructured interfaces for higher photocarrier generation and 2) developing tandem cells to increase the absorption in the visible/near-IR portion of the electromagnetic spectrum. Forrest and co-workers have been at the forefront of trying to optimize charge-generation via nanostructuring.\textsuperscript{43,44} Their work included the development of nanostructured copper phthalocyanine donor layers with a novel deposition technique called \textit{Organic Vapor Physical Deposition} (OVPD). This resulted in needle-like formations of CuPc leading to an increase in interfacial contact area between the donor and C\textsubscript{60}. This results in a ca. doubling of the efficiency when compared to a small-molecule bulk-heterojunction system. The other major advance in small-planar heterojunction technology has been that of tandem cell architectures. Hiramoto and co-workers stacked two cells using a perylene derivative and H\textsubscript{2}Pc using gold as the interlayer.\textsuperscript{45} They achieved a higher open-circuit photopotential, which was to be expected since the cells are stacked in series. Other developments came from Forrest and co-workers,\textsuperscript{46} who stacked multiple cells to increase the $V_{OC}$ more than 2x, and from Xue and co-workers who developed novel interlayers based on metal-organic doped systems.\textsuperscript{47}

There have been many advances in small-molecule planar-heterojunction systems since their inception nearly 25 years ago. The ability to finely tune the deposition process has resulted in devices with efficiencies over 5%. Further, it has become clear that
breaking the efficiency barrier of 10% will require an analytically rigorous understanding of the interfaces in these devices, particularly as seen in this work, the oxide/organic interface. This interface is limited in performance due to the high variability of the state of the oxide used during processing. In the following, a review of metal oxides, their basic science and processing will be covered.

1.5 **Transparent Conducting Oxides (TCOs) in PV Technologies**

The role transparent conducting oxides (TCOs) play in photovoltaic systems is crucial to device operation. This is due to the effects of sheet resistance, absorbance coefficients, and surface conditions, as well as being part of the charge-collection mechanism.\(^{48}\) In addition to its role as a bottom or top contact, use of TCOs has expanded into recombination interlayers for stacked multi-junction architectures and modifiers of current collecting electrodes to enhance charge-collection abilities. There are a limited number of viable thin-film oxides that fulfill the requirements for practical PV technology. These include indium-tin oxide (ITO), intrinsic and doped zinc oxide (ZnO: Al-ZnO), tin oxide and doped analogues (SnO\(_2\):Zn\(_2\)SnO\(_4\):Cd\(_2\)SnO\(_4\)), and titanium oxide (TiO\(_2\)).\(^{49}\) Each oxide has its own surface chemistry and optimal processing conditions. What links many of these systems together, however, is their charge-carrying abilities, optical properties, and sometimes, compositional makeup. The following section will cover some of the fundamental science, processing methods, and challenges posed by TCOs, with a small review on how improving performance has been accomplished.
1.5.1 Fundamentals of TCOs

1.5.1.1 Compositional

Metal oxide systems for PV applications are classified as semiconductors due to the nature of their band structure. They have both a conduction (CB) and valance band (VB) with an energy gap and Fermi level in between. These bands arise due to the many electronic levels that form as individual atoms begin to bond and form a crystal lattice. The size of the gap between the VB and CB determines the ease of which charge carriers can be generated and therefore the properties of the material under illumination (Figure 1.11). The energy gap for a typical TCO is approximately 3 eV at room temperature in the undoped state, with any value less, classifying it as an intrinsic semiconductor.49

\[ E_{\text{VOC}} \]

\[ E_{\text{Fermi}} \]

Metal Semiconductor Insulator

Type of Material

Figure 1.11: Band structures of a metal, semiconductor, and insulator, where the ability of the material to transport charge decreases going from left to right within the figure.
Doping of these films allows for free carriers to move about in the bands with relative ease, which in the case for most TCOs used in PV applications, moves the Fermi level towards the conduction band to create $n$-type semiconductors.

Doping of the oxide system can be achieved through a number of ways, the first of which is through the creation of oxygen vacancies. This typically occurs by annealing the oxide film in an inert atmosphere or by growing it in conditions in environmental conditions with low oxygen partial pressure. The vacancies provide extra carriers in the form of dangling bonds and therefore raising the carrier concentration level. The second way to raise conductivity is through the use of extrinsic dopants whose ionization energy is close to the conduction band of the oxide system. These extrinsic dopants subsitutionally reside within the host oxide lattice providing additional donor levels for conductivity. As it was pointed out by Fortunato and co-workers, the conduction mechanism for oxides that have been extrinsically doped is not based on ionic conductivity due to the immobilization of the ions within the lattice at room temperature.

1.5.1.2 Electrical Properties

The electrical properties of TCOs can be reported in a number of ways, the most convenient being sheet resistance which includes thickness within the measurement. The application of an electric field $E$ to materials like TCOs will result in the generation of a current whose quantity is defined as $J$. These two terms are connected via electrical conductivity $\sigma$, which can be expressed as: 
The reciprocal of the electrical conductivity gives the electrical resistivity $\rho$. If the material is designated to have dimensions $a$ for length, $b$ for thickness, and $c$ for width, then resistance is defined as:

$$ R = \rho \left( \frac{a}{bc} \right) \quad (1.4) $$

$$ R = \frac{\rho}{b} = R_{\text{sheet}} \quad (1.5) $$

If the length and width of the material are the same, the resistance is simplified to $R_{\text{sheet}}$, also known as the sheet resistance. This quantity is independent of the size of the square and is expressed as ohms/square ($\Omega/\square$). Sheet resistances for the oxides mentioned above range from 15 to 150 $\Omega/\square$ for thin-films with thicknesses below 200 nm. The other important measure of electronic materials properties is mobility. The conductivity of a thin-film is related to the mobility of charges via (4):

$$ \mu = \frac{\sigma}{Ne} \quad (1.6) $$

where $\mu$ is the charge carrier mobility, $\sigma$ is the electrical conductivity of the material, $N$ is the number density of electrons, and $e$ is the electron charge. Mobility is a useful measure for determining the ability of a material to transmit charge across an area under a defined electric field. Mobilities are directly proportional to the relaxation times of carriers, and their mean free path of within the solid. All these co-dependent properties are affected by a number of charge scattering mechanisms. There are 1) lattice scattering mechanisms, which depend upon solid state acoustic and optical modes, 2) neutral impurity scattering mechanism, which derive from non-participating species, 3) ionized impurity scattering,
resulting from the influence of the impurity of the electrostatic field surrounding it, and
4) electron-electron scattering, arising from collisions between the carriers themselves. If
the system is amorphous, additional scattering mechanisms arise from grain boundaries
due to the high number of interface states that can act as charge traps. This further leads
to space-charge regions and Schottky barrier heights inhibiting the flow of charges.51

This work will focus on the electrical properties of ITO due to its almost exclusive
use in organic photovoltaics research to date. Tin-doped indium oxide (ITO) retains the
crystal structure of indium oxide (In₂O₃) where the difference is: 1) larger lattice
constants in the bixebyite lattice and 2) the replacement of In³⁺ atoms with Sn⁴⁺ atoms.50
It has been reported that the difference in lattice constants is strongly dependent on the
preparation method of the ITO. It should be noted that ITO is truly composed of phase-
segregated regions of In₂O₃ and sub-stoichiometric tin oxide crystals rather than a truly
homogeneous system. ITO is usually doped to a Sn:In atomic ratio of ca. 1:10, with
oxygen vacancies ‘added’ throughout the structure. The combination of tin atoms (a one
electron donor level) and oxygen vacancies (a two-electron donor level) results in the
creation of energetically shallow electron donors just below the conduction band of the
oxide, due to the stabilization of the Sn:5s level (Figure 1.12).50
Electrons in these donor states can be easily promoted to the conduction band at room temperature leading to relatively high conductivities without loss of transparency, thus making ITO the most important transparent conductor in a wide variety of device applications. The theoretical band structure shows that electron-electron and electron-impurity scattering lower the bandgap energy in the film. Despite the promising qualities of ITO with respect to conductivity and transparency, several problems arise once it is used in technological applications in which substantial current densities are passed, as is discussed in Section 1.2.3.

Figure 1.12: Inset (A) shows the assumed band structures of tin-doped indium oxide and indium oxide for reference, where $E_g0$ denotes the direct bandgap, $W$ is the difference between the conduction band minimum and the valance band maximum. Inset (B) shows the energy band model of lightly Sn-doped In2O3. The band model shows that occupied Sn 5s levels lie close to the conduction band minimum (within a few kT in energy), as do the electron-rich oxygen vacancy sites. [Reproduced from reference 50]
1.5.1.3 Optical Properties

The absorption characteristics of transparent conducting oxides are dominated by two properties: 1) the bandgap of the material, which controls the extent of absorbance across the visible and near-IR and 2) the reflectivity, which controls the absorbance near the longer wavelengths and is dependent upon free carrier concentration. A typical transmission spectrum of a TCO (ITO) is shown in Figure 1.13. Information from optical measurements can be used to derive fundamental constants like refractive index and the bandgap of the material. Tuning of the transmission can be accomplished by reducing or increasing the carrier concentration. However, this is at the cost of narrowing the transmission window as the carrier concentration increases.

Figure 1.13: Transmission spectrum of tin-doped indium oxide on glass (90:10), showing the absorption just below 400 nm and transmission above that energy.
1.5.2 The Processing of TCOs.

1.5.2.1 Growth Processes for Oxides

Practical schemes for the production of thin-films of transparent conducting oxides vary widely. The growth of TCOs by one particular deposition technique can yield significantly different properties as opposed to other techniques due to the dependence of structural, electrical, and optical properties on film chemistry. The desire to control these three film properties has resulted in the development of techniques that rely mostly on clean vacuum deposition. As it will be seen, however, the tools that have evolved recently has allowed for low vacuum or atmospheric pressure processes. The techniques used for the deposition of TCOs are as follows: 1) Chemical Vapor Deposition, 2) Spray Pyrolysis, 3) Vacuum Evaporation, 4) Energy-assisted Deposition, 5) Sputter Deposition, and 6) Solution Deposition. Of all the techniques listed, only two of them do not occur in vacuum environment. This presents a challenge in terms of capital costs and thus, it is one of the reasons why the focus has shifted toward controlling the deposition of TCOs using non-vacuum techniques.

Chemical Vapor Deposition (CVD) makes use of organometallic species whose ligands are readily removed via a chemical or thermal reaction at the surface of a desired substrate. There are many variants to this technique, such as plasma-enhanced CVD, where a plasma discharge acts to induce dissociation prior to striking the substrate. In addition, Atomic Layer Deposition is similar to CVD, where metal chlorides or alkyl-metal complexes or other water-sensitive groups are deposited sequentially with water to create highly ordered metal oxide systems. For quick and large-scale application, Spray
Pyrolysis is the method of choice. This method sprays a mixture of metal containing compounds, like metal chlorides, and water onto a pre-heated substrate via an inert gas. The reaction of the metal chlorides with water forms the metal oxide and the uniformity and quality of the film are controlled by the size of the water droplets from the spray nozzle. Vacuum Evaporation uses a Knudsen-cell type of mechanical assembly that sublimes the material of interest onto a substrate. Energy-Assisted Deposition combines two technologies: Electron-Beam Deposition and Pulsed Laser Deposition. Both techniques make use of striking either the powder form of the metal or metal oxide with an incident electron beam, with subsequent deposition onto a substrate. Despite the development of the many techniques mentioned above, the most widely used are Sputter Deposition for its ease and controllability and Sol-Gel Deposition for its non-vacuum processing properties.

1.5.2.2 Processing via Sputter Deposition

Sputter deposition is currently the most common way to make TCOs across large areas. It is the method of choice in many PV manufacturing efforts for its stability, repeatability, and reliability. A typical sputtering system is shown in Figure 1.1. The setup is typically enclosed in a stainless steel vacuum chamber with the substrate holder opposite to the sputtering target. The target is comprised of either the metal oxide of interest or a predetermined mixture of the metals that are compositionally within the TCO. The target is mounted onto a Sputtering Source which is comprised of a cathode, anode, and permanent magnet used to support the plasma discharge at low pressures. An
inert gas (argon), or more typically a mixture of the gas with oxygen backfills the chamber under vacuum (mTorr). A plasma is generated yielding a high concentration of positively charge atoms. Under the influence of the magnetic field from the sputtering gun, the number of collisions incident on the target increase due to an increase in the mean free path of the electrons. The collisions between the charged gas atoms and the target result in momentum transfer of the target atoms towards the surface of the substrate. Fine control of the partial pressures of the reactive gases yield TCOs whose composition can be tailored to any desired ratio. Post-deposition annealing aids in

Figure 1.14: Cross-sections of a typical sputtering system used for creating transparent conducting oxide thin-films. The processes involves the backfilling of the chamber with either argon or argon/oxygen mixtures. A plasma is initiated, resulting in momentum transfer from the gas to the target due to the localized magnetic field within the sputtering gun. The atoms from the target diffuse to the substrate below.
increasing oxygen vacancies and/or reducing the amount of grain boundaries, associated with some systems, thereby increasing conductivity.

1.5.2.3  Processing via Solution Deposition

The appeal of using non-vacuum techniques for TCO fabrication does not derive solely from simplicity, but also from an economic incentive. As mentioned above, the techniques that make use of vacuum require pumps, engineering controls, and many other pieces of equipment that are costly. The solution deposition methods developed in the past few years required significantly less in terms of technological sophistication and capital. The most popular of the methods is sol-gel deposition via spin casting. In this method, a metal alkoxide is dissolved in a solvent (typically an organic solvent and water) and dropped onto a surface that is revolving at a set rotation rate. The result is the formation of thin-films whose thickness is controlled via the spinning rate, concentration of precursors in solution, and amount dropped onto the substrate.58

1.5.3  Intrinsic Problems with the TCO Surface Chemistry

1.5.3.1  State of the Surface and its Reactions

The near-surface region of TCOs is comprised mainly of metal-to-oxygen bonds, vacancies, and hydroxylated components.50,59,60 The susceptibility for surface reaction varies widely amongst TCOs. This variability is impacted by the surface concentration of vacancies, defect density, and dopant concentration. Indium-tin oxide is one TCO that is highly sensitive to atmospheric exposure, where tin and indium hydroxides populate the
surface with additional carbonate species from ambient CO$_2$. This model was derived from the work of Brumbach and co-workers who sputter deposited ITO thin-films and analyzed the surface via X-ray photoelectron spectroscopy to determine the evolution of adventitious contaminants as a function of atmospheric exposure. In addition, solution electrochemistry was used to determine rates of electron transfer on different pre-treated surfaces of ITO. It was found that pre-treatment of the surface increased the performance of the electrode overall due to contamination removal, therefore concluding that these contaminants also contribute to impeding the performance of the ITO electrode.

Following the work of Brumbach and co-workers, Marrikar et al. investigated the growth of conductive polymers on various pre-treated ITO surfaces. Their results showed that growth of the conductive polymer was more prominent when the ITO surfaces were activated with aggressive acid-etching and plasma processes. Based upon electron transfer rates obtained from these different pre-treated surfaces, estimations of the percentage of blocked sites were calculated based on a model first proposed by Amatore and Savéant for electrodes composed of arrays of microelectrodes. Their analysis pointed to a high amount of blockage with detergent/solvent cleaned ITO, which would drop following pre-treatment. Knowing that these ITO surfaces are severely underperforming even after pre-treatment using detergents and solvents, many methods for alleviating this problem have been developed, which are: 1) wet chemical processing, 2) dry processing, and 3) surface modification. These are discussed below.
1.5.3.2  

**Surface Pre-Treatments: Wet and Dry Processing**

Indium-tin oxide has been the TCO of choice for display devices due to its high conductivity, good optical transmission window, and the ease in fabrication required to create reliable electronic devices. M. Scholten and J.E.A.M. van den Meerakker published the two most important studies in the wet processing pre-treatment of ITO.\(^{63,64}\) The first dealt with understanding the role of halogen-based acids in the etching process.\(^{63}\) Through a series of experiments in which various acids (e.g. HBr, HCl, HI) were used to etch DC sputtered ITO, they identified various etching rates. The most aggressive of the etching schemes involved a mixture of HCl and FeCl\(_3\), where it was proposed that the halogen attacks the indium-oxygen bonds, while the FeCl\(_3\) catalyses the reaction. The second work focused on understanding the kinetics of this etchant.\(^{64}\) Their results show that the rate of dissolution of polycrystalline ITO is first order in which the breaking of H-Cl and In-O bonds occurs while the formation of In-Cl and O-H takes place. In agreement with their initial studies, they determined that FeCl\(_3\) acted only as a catalyst during the etching process.

In addition to wet processing methods, dry procedures utilizing plasmas have also been investigated. The first successful application of a dry processing method with uniform results for flat panel displays was demonstrated by Shih and co-workers.\(^{65}\) Their work in planar inductively coupled plasma systems provided a reproducible etch process for ITO and other thin-films of interest. Following this development, the application of a dry method in organic electronic devices is credited to Wu and co-workers,\(^{66}\) where oxygen plasma pre-treatment resulted in higher performing OLEDs when compared to
non-plasma treatment. The processing techniques mentioned above have been important in the advancement of device performance in many applications. Despite the relative expansion of capabilities provided by such processes, they do not necessarily allow for full tunability of the surface energetics to maximize compatibility between many systems of interest (e.g. the oxide/organic interface). Surface modification of ITO allows the ability to access a full range of tunability due to the ease of functionalization via synthetic methods and simple chemistry.

1.5.3.3 Surface Modifications via Small-Molecule Chemisorption

ITO surface modification with polymers, small-molecules, and metals is an area of research that has been intensely investigated. The surface of ITO exposed to the ambient atmosphere is typically hydroxylated and covered with adventitious contaminants. As a result, tailoring of the surface chemistry is trivial due to the simple condensation- or substitution-type modifications that can be performed using small-molecules with the proper reacting end groups. Silanes, carboxylic acid, and phosphonic acid chemistries are employed for surface modification (Figure 1.15). Surface modification via silane chemistry employs the use of alkoxide or halogen ligands to react with hydroxyls on the surface. This creates a metal-to-oxygen-to-metal bond that generates alcohols or hydrogen halides as byproducts. Carboxylic acid and phosphonic acid chemistry employ the same mechanism, in which a condensation reaction between two hydroxyls generates one unit of water. The use of phosphonic acid modifiers on ITO has been investigated by Paniagua et al. via a combination of surface sensitive...
techniques. Their application of potential modulated infrared reflectance absorbance spectroscopy (PM-IRRAS), along with photoemission studies and contact angle measurement, showed that the work function of the ITO can be modified. Furthermore, the phosphonic acid was found to bind preferentially in a bidentate mode, showing strong adhesion to the ITO surface. Others like Sharma and co-workers and Schulmeyer et al. have shown that these chemistries can be applied to a range of metal oxide systems and electronic devices with relatively high success.

The ability of transparent conducting oxide materials to transmit light while allowing charge carriers to flow with relative ease has made them a target for further improvement and intense research. Despite these advantages, many problems still face these oxide materials.

Figure 1.15: Basic model for metal oxide modification with small-molecule modifiers such as silanes, carboxylic acids, and phosphonic acids. All modifiers exploit the use of surface hydroxyls in order to create a chemisorption event.
systems, especially when applied in photovoltaic systems. These problems arise from the ability of these oxides to readily react with their surrounding environment, leading to surface contamination that inhibits efficient charge collection. Remedies to these problems have been attempted using wet, dry, and chemical processing with varying degrees of success.

1.6 Gold Nanoparticles on Oxide Surfaces

1.6.1 Metal Oxide-Supported Gold Nanoparticles-Review

1.6.1.1 Historical Background

Metal oxide-supported gold nanoparticle research has been ongoing for nearly 40 years. The original pioneers of this work were Bond and Parravano et al.\textsuperscript{70,71} Their investigations in the catalytic conversion efficiency of CO to CO2 using a series of oxide-supported Au-NPs. Later, Haruta and co-workers followed by developing a number of methods to create supported gold nanoparticles from different metal oxide systems (Figure 1.16).\textsuperscript{72,73}

Their methods included 1) sputtering, in which a target of the desired metal oxide along with a gold target was co-sputtered, 2) co-precipitation, where HAuCl\textsubscript{4} and a metal nitrate were poured in an aqueous solution of sodium carbonate yielding the mixed metal oxide precipitate, 3) deposition precipitation, in which an aqueous solution of HAuCl\textsubscript{4} was taken to a high pH and the metal oxide was added, followed by calcinations, and 4) CVD, where an organometallic complex of gold was introduced onto a metal oxide surface, followed by calcination.
1.6.1.2 Catalytic Activity of MOx-Supported Gold Nanopaticles

MOx-supported gold nanoparticles are very reactive towards many of the important industrial gases used in oxidation and polymerization processes. This catalytic activity has prompted many researchers to investigate the reasons into this phenomenon using a variety of approaches. The studies on understanding the fundamental aspects of this catalytic activity have been concentrated in three areas: 1) variation in the size and shape of the clusters, 2) variation in preparation methods, and 3) variation in the oxidation state of the particles. Valden et al. tried to determine if a link existed between the size of the gold nanoparticles and their catalytic activity. Gold clusters ranging from 1 to 6 nm were deposited on single-crystal titanium dioxide surfaces, and studied by photoemission spectroscopy, microscopy, and adsorption measurements. Their results show that activity...
is at its highest with gold islands containing two equivalent monolayers of gold. This was attributed to a quantum-size effect of these clusters whose bandgap is uncharacteristic of the metal.

Guzman and co-workers conducted a series of studies in which they created specimens with varying amounts of oxidized gold oxides, which were then correlated with their catalytic activity.\textsuperscript{76,77} Using spectroscopic methods and adsorption studies, the work showed that there is a link between the presence of these cationic species on the surface and CO reactivity. In addition to these discoveries, there was compelling evidence that pointed to one parameter (size, oxidation state, etc.) or the other being responsible for this activity. As it was best summed up by Davis,\textsuperscript{77} the definitive answer in determining the activity might not be necessarily dependent on one single variable, but rather on a compilation of many factors. The next section focuses on understanding the deposition-precipitation mechanism more thoroughly due to its role in this body of work.

1.6.2 Deposition-Precipitation Protocol for MOx Au-NPs

1.6.2.1 Chloroauric Acid: Properties and Behavior in Aqueous Media

Chloroauric acid (HAuCl\textsubscript{4}) is a metal halide which readily ionizes when placed in an aqueous environment. The dissociation in aqueous media leaves a net negative charge whose ligands are readily interchanged with hydroxyls and water depending on the pH of the solution and ionic strength. A high pH of (>8), which is the range where nanoparticle deposition is preferred due to creation of small particles (<10 nm),\textsuperscript{78} two types of species can exist, a charge-neutral Au(OH)\textsubscript{3} or a charge-negative Au(OH)\textsubscript{4}.\textsuperscript{−}
The existence of these species is solely dependent upon the concentration of chloride ion species within the solution. As the predominance diagram in Figure 1.17 shows, the difference between the generation of the neutral or charged species is set at a chloride concentration of $1.3 \times 10^{-4}\text{M}$. Many researchers have based their work on the assumption that charged species, as opposed to neutral, are generated. This is an important distinction to make due to the possible mechanisms that can be derived for the formation of gold nanoparticles on oxide surfaces.

![Predominance diagram showing the various species of chloroauric acid that form in solution as a function of pH and chloride ion concentration, based on reported equilibrium constants for mixed species. The boundaries represent the conditions in which species are equal in concentration.](Reproduced from reference 79)

**1.6.2.2 Metal Oxide-Supported Gold Nanoparticles**

The deposition mechanisms of Au-NPs on oxide substrates have not been extensively studied. Moreau et al. attempted to develop a model for the creation of Au-NPs on TiO$_2$. Considering the many factors that affect deposition, such as temperature, concentration, pH, and time, a series of TiO$_2$-supported gold nanoparticle samples were
created. It was assumed that the gold species in the deposition solution at a high pH was charged $[\text{Au(OH)}_4^-]$, leading to a mechanism which depended on the dissociation of the negative species into a neutral one, followed by a series of condensation reactions with surface hydroxyls (Figure 1.18).

Progression of the condensation reactions was hypothesized to form a metal oxide network, which was known to be unstable above room temperature.$^{82}$ Hugon et al. attempted to address the deposition-precipitation mechanism via the reduction of urea under the presence of heat, which slowly raises the pH.$^{83}$ This work showed that this method deposited all of the gold on the surface of the oxide, confirming previous results, where it was postulated that a gold-hydroxide complex binds to the surface via surface hydroxyls. The length of deposition affected the loading density and fragmentation of the particles onto the surface of the oxide. These two studies on the deposition-precipitation mechanism have given a possible path for the creation of gold nanoparticles on the surface of TiO$_2$ and have linked gold species present during deposition mechanism to specific reaction pathways.

Figure 1.18: Proposed mechanism for gold nanoparticle formation under a negatively charged surface proposed by Moreau and co-workers. The mechanism relies upon the dissociation of the charged species, which then binds to the surface through a condensation reaction, ultimately leading to an oxidized species that readily decomposes upon heating. [Reproduced from reference 80]
1.7 Titanyl Phthalocyanine: Properties and Applications

Titanyl phthalocyanine is a photoconductor that has been of interest for many years due to its xerographic properties that derive from its charge-generating abilities. It is tetravalent with oxygen bonded to the titanium atom (Figure 1.19). It has very strong absorption coefficients in the visible to near-IR region, whose absorption maximum (Q-band) can shift based upon the structural organization of the bulk system. As a result of these properties, phthalocyanines have been used extensively in other technologies such as photovoltaics, sensors, transistors, and even as photodynamic therapy agents. The following section will cover the properties of TiOPc relevant to its use in photovoltaic systems.

1.7.1 Structural and Electronic Properties of TiOPc

1.7.1.1 Structural Aspects

Figure 1.19: Image of titanyl phthalocyanine, where the oxo-titanium bond extends out of the plane of the molecule, where the geometry forces the molecule to arrange itself in the bulk like that seen in Figure 4.1.
Titanyl phthalocyanine can arrange itself into various special positions with respect to adjacent TiOPc molecules. These differences tend to be relatively small distance-wise but result in significant differences spectroscopically. Structure parallel to the molecular plane leads to the common convention for naming: i) convex pairs, where the oxo-titanium bonds are facing each other and ii) the concave pairs, where the oxo-titanium bonds face away from each other. Observation perpendicular to the molecular plane leads to observed differences in the interactions between the oxo-titanium portion of the molecule, the $\pi$-systems on the periphery, and the nitrogen atoms.

These differences are grouped into classes of polymorphs or phases whose properties vary depending on the class. These phases of TiOPc are structurally grouped into four classes: the as-deposited, Phase I, Phase II, and Phase-Y. Hiller and co-workers were the first to determine the structure of Phase I and Phase II TiOPc (Figure 1.20). The main difference between these two phases derives from 1) the significant overlap between the
π-systems on the periphery of the structure and 2) the reduced cell volume. This leads to a significantly higher strained system in the Phase II relative to the Phase I.

Fujimaki and co-workers were the first to discover an additional polymorph using a series of ball milling and solvent treatments, which was denoted as Phase-Y. Their results showed very high photo-electrical activity in the near-IR, low dark decay, and overall cyclic stability. Oka and co-workers characterized the structure of the Phase-Y polymorph using x-ray diffraction. Their results showed that the positioning of the Pcs in this polymorph are similar to that of the Phase I polymorph. The only difference arose in the tilt between molecules along the $a$-$b$ plane of the unit cell, where a 4° tilt leads to a void along the $a$-$b$ plane, as opposed to a 19° tilt in Phase I polymorph. The description of the various polymorphic structures of TiOPc led to efforts to understand the relationship between structure and thin-film electronic properties. The results from this work showed a direct relationship between the photoactivity of the system and the structural strain experienced by the individual molecules within the bulk.

The polymorphs of TiOPc can be grown in a number of ways, such as slow evaporation rates from a Knudsen cell-type of apparatus, deposition on modified surfaces that induce the formation of one phase over another, deposition on pre-heated substrates and the most important, solvent-annealing with high vapor pressure solvents. Due to the ease and low cost of this last method, it has been investigated most intensely. Conboy and co-workers investigated the morphological impact on thin-films of TiOPc treated with various solvents. They concluded that upon solvent-annealing, the films compress significantly, forming long-range crystallites on the substrate. Others like
Del Cano and co-workers investigated the effect of solvents and heated substrates on various phthalocyanines\textsuperscript{97}. Their results showed that visible light absorbance shifts towards the near-IR, indicating important electronic properties are being changed based upon structural changes.

1.7.1.2 Electronic Aspects

Structural and crystallographic changes within the TiOPc films give rise to some notable differences in measurable electronic and optical properties (Figure 1.2\textsuperscript{1}). The molecular symmetry of TiOPc changes ($C_4v$ to $C_1$) as it goes from the solution to the solid state. This results in the lifting of the degeneracy of the LUMO states into two components: i) the blue-shifted absorption peak (LUMO+1) and ii) the red-shifted absorption peak (LUMO). As the structure in the solid state begins to strain even further (e.g. as-deposited to Phase I to Phase II), splitting of the LUMO states become greater.

Mizuguchi et al. were the first to try to link the relationship between the structural and electronic properties of TiOPc\textsuperscript{99}. Using a series of Phase I and Phase II single crystals, computational methods for structural determination, and temperature dependent optical measurements, they concluded that the change in optical absorbance can be traced to the strain within the structures, which leads to two $\pi-\pi^*$ optical transitions. Their temperature dependent absorbance studies led to the conclusion that shifting of the main transition peaks in the Phase II towards the red under low temperatures was due to modified contact along the molecular stack being the structural change dominating the optical characteristics.
Nakai and co-workers proposed that molecular distortions alone cannot account for these changes in the solid-state spectra.\textsuperscript{100} They considered several origins for these optical characteristics, mainly excitons, charge-transfer phenomena, and molecular distortions. They began by first trying to reproduce the spectra (liquid and solid) by using single molecules, aggregates, and bulk structures via computational methods. Their results showed that the near-IR transitions originate from large charge-transfer character within the system, along with large molecular orbital overlap for the TiOPc molecules throughout. Yamaguchi et al. used electric-field-modulated picoseconds time-resolved florescence spectroscopy to evaluate the character of the excited state in the near-IR, which agreed with the results of Nakai and others on the nature of the excitonic state within that transition.\textsuperscript{101,102}

![Figure 1.21: Visible spectra of the various polymorphs of TiOPc. As pointed out by Mizuguchi and co-workers, the splitting of the LUMO states (LUMO and LUMO+1) increases as a function of the overlap between adjacent molecules.](image)
1.7.2 Photovoltaic Device Development with TiOPc

The first photovoltaic devices developed with TiOPc were reported by Tsuzuki and co-workers, who created planar heterojunction photovoltaics using \( N,N\text{-Dimethyl-3,4,9,10-perylenediyldicarboximide} \) (C1-PTCDI) as the electron acceptor. They produced a series of devices that were solvent-annealed by ethanol for varying amounts of time. Their results showed that solvent-annealing improved device performance and concluded that this performance results from the increased absorbance in the near-IR. Tsuzuki et al. attributed the increase to the highly photoactive transition in the near-IR.

Brumbach et al. created planar heterojunction OPVs using TiOPc and C\(_{60}\) as the acceptor. In addition to creating the devices, the researchers sought to correlate photoemission spectroscopy data with the performances seen in the photovoltaic devices. Their results showed that good predictions on the open-circuit photopotential could be made using this technique, and that this system accounted for one of the largest open-circuit photopotentials seen in the literature.

1.8 Dissertation Overview

The body of work presented within this dissertation has resulted from studies into the chemistry of the metal oxide/organic interface in small-molecule planar-heterojunction photovoltaic devices. Initial inquiries were made into the effects of metal nanoparticle modification on the surface of ITO and how it affected charge-transfer in OPV devices, which is covered in Chapter 3. From these inquiries, it was noticed that improvements were made in charge collection using TiOPc as a donor material. The investigations into
the basic science of this interface led to the discovery of the change in polymorphism within TiOPc as it was deposited over these modified surfaces, as described in Chapter 4. The polymorphism of TiOPc in photovoltaic devices was investigated via the optimization of the processing conditions in order to make effective, high performing devices with higher ordered polymorphs. The study of performance losses in the device and the role of surface structure at the interface led to the work presented in Chapter 5, where the degree of co-facial overlap between the donor and acceptor and how it affected device performance was investigated.

*Chapter 3* discusses the modification of ITO with gold nanoparticles and its effects on the performance on small-molecule photovoltaics. In an attempt to address the problems associated with ITO, whose surface is highly contaminated due to its reactivity with atmosphere, gold nanoparticle modification was carried out using a solution method developed originally for oxide modification for use in carbon monoxide catalysis.

*Chapter 4* focuses on the role of the titanyl phthalocyanine polymorphs within planar-heterojunction photovoltaics and the basic science governing the behavior. The use of various polymorphs of TiOPc and their role in photoelectrical activity was investigated with the goal of understanding the link between structure and performance.

*Chapter 5* sought to understand the role of co-facial interactions at the donor/acceptor interface in the operation of planar-heterojunction devices. Two perylene dyes (perylenetetracarboxylicdianhydride, PTCDA and perylenetetracarboxylicdianhydride-N,N'-bis(butyl)imide, C$_4$-PTCDI) were used as electron acceptors while TiOPc was used
as an electron donor to monitor device performance and to try to correlate device behavior with the structure at the organic/organic interface.

Chapter 6 summarizes the major achievements that have been accomplished within this work and focuses on suggestions on how to continue to improve the performance of organic photovoltaic devices through interfacial studies in future experiments.
CHAPTER 2: EXPERIMENTAL

2.1 Testing Organic Photovoltaics

2.1.1 Current-Voltage Characterization

All the photovoltaics in this work are evaluated by the same procedure. An image of the testing platform used for the measurements in this dissertation is shown in Figure 2.1.

Figure 2.1: Image of the testing station routinely used for device testing. Included in this setup is a 300W xenon arc lamp, a filter wheel with a series of neutral density filters for light intensity control, a holographic diffuser, and the necessary electronics to test devices.

For I-V (current-voltage) measurements, the voltage of a cell with a defined area is swept prior to light exposure while the current is monitored with a source meter. During data collection, parameters such as the dark current density ($J_0$), the parallel resistance ($R_p$ or $R_pL$ under exposure to light) and the series resistance ($R_s$ or $R_sL$ under exposure to light) can be extracted from the measurement (Figure 2.2).
After testing in the dark, the cell is placed in front of a light source which closely matches the spectrum of the sun. The most common light source used for this application is a xenon arc lamp, which exhibit many of the features of the spectrum of the sun, where the energy decays as the wavelength moves into the infrared red (IR) (Figure 2.10). In order to decrease the intensity of the near-IR from the lamp, an attenuating filter is placed in between the lamp and device, usually denoted as an *Air:Mass* filter. The standard spectral output used for solar cells is approximately 100 mW/cm$^2$, denoted as the AM 1.5G, and shown spectrally in *Appendix A*.

Under exposure to light, several parameters are extracted from the I-V measurements. The most important of which are: the open-circuit photopotential ($V_{OC}$) which represents the point where the charge-carrier recombination is equal to the optical charge-carrier generation, the short-circuit current density ($J_{sc}$) where the maximum amount of current is extracted under no applied potential, the fill factor ($FF$) which represents the ratio of...
the product between voltage and current at the maximum power point and voltage and current at the theoretical maximum power point and the efficiency ($\eta$) which is just the product of all three factors divided by the incident power. Figure 2.3 represents the theoretical positions of the energy levels as a function of the $I$-$V$ curve location for organic planar heterojunction PVs. Evaluating the performance under no light, we observe Point 1 at high forward bias. In this segment, there is a relatively high amount of energy that is being put into the system from the external source meter, which is the energy regime where solid-state lighting devices (LEDs) operate under. Observing the energy diagram, the acceptor and donor systems are poised to accept charges that recombine at the interface dissipating the energy as heat or light emission. Moving

Figure 2.3: Hypothesized potential across the top and bottom contact in a planar-heterojunction photovoltaic device as a function of bias. Points of interest across the dark and the light curves are highlighted.
towards Point 2, where there is no bias ($J_0$), a steady-state condition is achieved where no net carriers are being generated or pumped into the system since the chemical potential of the electrodes are higher with respect to vacuum than those of the adjacent semiconductors.

Under the influence of light the same processes as in the dark are taking place, but with additional charge carriers resulting from the photogeneration process. Point 1 represents the illuminated device under high forwards bias and light. In this case, there is a net input of energy taking place with excess excited states that recombine as quickly as they dissociate due to the lack of a preferential electric field where the carriers can migrate, therefore leading to excess energy in the form of heat. Moving towards a smaller positive potential ($V_{oc}$), Point 3 represents the open-circuit photovoltage. At this point, there is no net input or output of current; the current which is being produced by the device under the influence of light absorption is matched by that which is being recombined. Point 4 exists under the influence of no field (0 V), where current generation is at its maximum and there is no influence from the external field to collect the carriers, and the process is determined by diffusion of the charge-carriers towards the electrodes. At extremely negative potentials, Point 5, the collection of charges is at its maximum where carriers that could not be extracted due to recombination are also collected.
2.1.2 Optical Characterization

Determining the current-voltage characteristics of an OPV only describes one aspect of performance light sources that might not be suitable for device testing can be used and lead to device parameters which are not representative of true values under standard testing conditions. It is now standard practice in the PV community to obtain External Quantum Efficiency (EQE) measurements, also known as Incident-Photon-Current-Efficiency (IPCE). Measurement of the Internal Quantum Efficiency (IQE), also known as Absorbed-Photon-Current-Efficiency measurements (APCE), is also a standard protocol used to determine the ratio of electrons that are produced as a function of absorbed photons (Figure 2.4).

![Figure 2.4: Dual plot of Incident-Photon-Current-Efficiency (IPCE - solid) and Absorbed-Photon-Current-Efficiency (APCE - dashed) measurements, along with the corresponding equations. IPCE is denoted as a percentage, since it is a measure of a ration between electrons that are collected and photons that are incident upon the surface. APCE is the measured of electrons collected per absorbed photons.](image-url)
External quantum efficiency is measured by exposing a cell to monochromatic light under short-circuit conditions. The current is collected as a function of wavelength, which through a series of calculations (see Appendix A) is converted to external quantum efficiency, simply described as the ratio of electrons that are collected to the number of photons that are incident on the cell. An image of the standard EQE testing setup is shown in Figure 2.5.

Figure 2.5: Instrumental setup for IPCE/APCE measurements. The components include a 300W xenon arc lamp, focusing optics, chopper for lock-in amplification, automated monochromator, iris, and hermetically sealed unit for device contact.

From this spectrum, back calculations of the current can be obtained to cross-check with I-V measurements (see Appendix C). Internal quantum efficiency is the result of dividing the absorbed photons obtained from transmission experiments by the IPCE response. Although this particular measurement does not take into account other optical parameters that are necessary for correct determination of APCE,\textsuperscript{103} it is a useful qualitative measure of photoactivity of absorbed photons within the system.
2.2 Experimental Methods

2.2.1 Sputtering of ITO Thin-Films

Indium-tin oxide thin-films with varying indium oxide-to-tin oxide ratios were sputtered via pulsed DC magnetron (Kurt J. Lesker, Model AXXIS). A base pressure below $10^{-8}$ Torr was reached, while the working pressure for the system was maintained at $2 \times 10^{-6}$ Torr. Several 1/8” thick by 3” diameter ceramic targets (Plasma Materials) were used, which were bonded to copper back-plates with indium paste. After deposition, thin-films were heated in vacuum to 300 °C for one hour and allowed to cool to room temperature. Afterwards, the thin-films were removed from vacuum, immediately followed by four-point probe analysis and allowed to equilibrate to atmospheric conditions (>24 hours) prior to XPS analysis and/or modification.

2.2.2 ITO Thin-Film Pre-Treatment

Commercial (Colorado Concept Coating LLC.) and sputtered indium-tin oxide coated onto glass with an approximate thickness of 150 nm and 250 nm gave a measured sheet resistance of $\sim 15 \ \Omega/\square$ for commercial thin-films and varying sheet resistances for sputtered thin-films (Figure 3.5) via four-point probe. Substrates were cut down to 1” x 1”, followed by rising with absolute ethanol. For photovoltaic devices, substrates were then treated with positive photoresist (Rohm and Haas) in order to create the desire ITO pattern, followed by subsequent steps required for effective patterning (i.e. exposure, heating, etc.). This was followed by etching with $aqua regia$ at a 3:1 ratio with the temperature set at 120 °C for a total etching time of $\sim 30$ s. Prior to use, pre-treatment of
substrates was carried out via the following method: 1) scrubbing with a microfiber cloth (Peca Products) and 10 % Triton X-100 (Alfa Aesar) for at least 20 s, 2) sonication in 10% Triton X-100 for 15 min, 3) rinsing with nanopure water, 4) sonication in nanopure water for 5 min, 5) rinsing with 200 proof ethanol (Decon Labs Inc.), and 6) sonication in 200 proof ethanol for 15 min.

2.2.3 Gold Nanoparticle Modification Procedure

Chloroauric acid (HAuCl₄, Aldrich) was dissolved in nanopure water in order to give the desired concentrations, which were 10⁻³ M for microscopy/photoemission analysis and 10⁻⁵ M for device fabrication. The pH was gradually adjusted with diluted ammonium hydroxide (Jones-Hamilton) until a pH of 9.0 +/- 0.1 was reached. The solution was then heated to 60 °C followed by the immersion of the oxide substrates under constant stirring. The length of immersion for the oxides that were analyzed via microscopy are described within the figures in Chapter 3, while for devices, a time of 2.5 hours gave the best results. A custom piece of glassware allowed for stirring of the oxide within a vessel while a condenser kept water from evaporating slowly (Figure 2.6). After immersion, substrates were removed and dried under a stream of nitrogen, followed by heating at 300 °C for one hour in atmosphere (Barnstead Thermolyne, Model 48000). Once heated, substrates were allowed to cool to room temperature, scrubbed with a microfiber cloth (Peca Products) and 200 Proof ethanol (Decon Labs Inc.), and finally sonicated in 200 proof ethanol for 5 min to remove additional physisorbed material. For control devices,
the same procedure was carried out with the exception of the chloroauric acid within the solution.

2.2.4 Synthesis of perylenetetracarboxylicdianhydride-N,N'-bis(butyl)imide, C₄-PTCDI

Perylenetetracarboxylicdianhydride (9.80g, 0.025 moles), 1,3 dicyclohexylcarbodimide (10.3g, 0.05 moles), and N-butylamine (7.4mL, 0.075 moles) were mixed with quinoline (2.5 mL) in a 100 mL roundbottom flask. The reaction was
allowed to reflux for approximately 20 hours at a set temperature of 238°C. The solution was allowed to cool, followed by the addition of methanol (40 mL). The solution was placed into a chemical refrigerator for three days. Following filtration, the crude solid was treated with 200 mL of 5% sodium bicarbonate for 30 min at 100°C. Once filtered, the solid was recrystallized from toluene and dried under vacuum at 100°C.

### 2.2.5 Device Fabrication

Prior to being introduced into the vacuum system (Figure 2.7), modified ITO substrates were removed from ethanol and dried under a stream of nitrogen. Treatment was followed with an RF-generated plasma (Harrick, Model PDC-32G) while compressed air was leaked for 10 min at an applied power of 10.5 W and an operating pressure of 400 mTorr. For devices used in Chapter 5, compressed oxygen was leaked for 8.5 min at the same applied power. Titanyl phthalocyanine, copper phthalocyanine (Aldrich), C$_6$0 (MER Corp.), PTCDA (Aldrich), C4-PTCDI, and bathocuproine (BCP,

![Figure 2.7: Vacuum deposition system used for the creation of organic photovoltaic devices.](image)
Aldrich) were vacuum sublimed (Figure 2.8) at least three times (with bathocuproine only sublimed twice) prior to use. Aluminum top contacts (Alfa Aesar) were deposited with 99.999% rated material. All organic materials were thoroughly degassed prior to deposition. The system base pressure was allowed to reach at least $8 \times 10^{-7}$ Torr before fabrication. Thin-films were deposited at a rate of approximately $1 \text{ Å s}^{-1}$ while being monitored with a 10 MHz quartz crystal microbalance (QCM-Newark) and a frequency monitor (Agilent, Model 53131A).

To generate various higher ordered polymorphs of TiOPc, a solvent-annealing protocol was developed. Solvent-annealing on different fractions of as-deposited TiOPc was carried out by placing the thin-films faced up, in closed containers (Nalgene 4 oz., 125 mL polypropylene) with either methanol (1 hour) or chloroform (3 hours) in a small glass vial. For example, 60% Phase X TiOPc thin-films (where $X = \text{II}$ or III-like) results from deposition of 12 nm of as-deposited TiOPc, conversion to the Phase X polymorph, followed by deposition of another 8 nm of as-deposited TiOPc. Top contacts were
deposited via thermal evaporation and monitored with a 6 MHz QCM (Tangydine) and deposition monitor (Inficon, Model 758-500-G1).

2.2.6 Device Testing

Current-voltage (I-V) measurements were obtained for at least six devices per substrate, with the best performing devices being represented in the figures. The geometry of the masking system allowed for a device area of 0.125 cm$^2$, while the bottom contact-to-top contact distances were fixed to the same distance, allowing for reliable averaged data acquisition (Figure 2.9). Measurements were carried out in a nitrogen-filled glovebox (MBraun) with water levels and oxygen levels <0.1 ppm. For the devices shown in Chapter 3, a 300 W xenon arc lamp (Newport) was used as a light source with an AM 1.5G optical filter (Newport) and engineered diffuser (Newport) used to attenuate

![Figure 2.9: Device testing holder showing the interconnects that make contact with the device [Inset (A)], along with a schematic of the device showing points of contact [Inset (B)]. The shaded area represents the active device area (0.125 cm$^2$).](image-url)
the output. For the devices shown in Chapter 4 and 5, a 250 W tungsten-halogen lamp (Cuda) was used as a light source, whose incident light was passed through a 950 nm short pass filter (Melles Griot) and a sandblasted diffuser (Edmund Optics). Data acquisition was carried out with a source meter (Keithley 2400) and in-house software (National Instruments Labview, version 8.2).

The potential was swept from -1.00 V to 1.50 V using a 5.00 mV step starting from the negative potential. The distance of the devices were adjusted in order to receive an incident power density of 100 mW/cm², which was calibrated with a flat-response thermopile (Newport, Model 818-P) and crossed-checked with a silicon photodiode (Newport, Model 818-SL). Further information on calculating incident power on the surface of the device can be found in Appendix A. Figure 2.10 shows the spectral distribution incident upon the devices during the course of experiments.

Figure 2.10: (1) Spectral irradiance for the 300 W xenon arc light source used, including the AM 1.5G filter at 100 mW/cm² and (2) the standard AM 1.5G profile.
Incident-Photon-Current-Efficiency (IPCE) measurements were acquired in an in-house fabricated hermetically sealed unit (Figure 2.11). Detailed schematics can be found in the Armstrong Lab Files. For the devices shown in Chapter 3, a 600 W quartz tungsten halogen lamp (Newport) was used as the light source. For the devices shown in Chapter 4 and 5, a 300 W xenon arc lamp (Newport) was used. The 250 Hz modulated light (Standford Research) was passed through an automated monochromator (Newport, Model Cornerstone), where the data was acquired at 4 nm intervals. Incident power and calibration of that power though the monochromator was measured with a silicon photodiode (Newport, Model 818-SL), while device measurements were acquired at short-circuit conditions. The resulting signal was inputted to a lock-in amplifier (EG&G, Figure 2.11: Visuals of the hermetically unit designed to test devices in atmosphere during IPCE measurements.)
Model 5209), while the output was fed into an in-house data acquisition system (National Instruments Labview, version 8.2).

### 2.2.7 Photoemission Spectroscopy

XPS measurements were carried out in a photoelectron spectrometer (Kratos, Model 165 Axis-Ultra) using a monochromatic Al Kα source at 1486.6 eV and a He(I) excitation source (21.2 eV) for UPS measurements. A –9.00 V bias was applied to the sample to further enhance the collection of lowest kinetic energy electrons for UPS experiments. The spot size for the XPS analysis was 300 x 700 µm while for UPS, spot size ranged between 1 – 3 mm. For XPS experiments, each corresponding energy region was scanned at least 20 times with a 0.1 eV step at a 20 eV pass energy, while regions for UPS experiments were scanned five times at 0.01 eV.

For variable temperature studies in Chapter 3, an un-heated substrate was pulled from solution after 60 min, dried under a stream of nitrogen, and then placed in the analysis chamber until the base pressure reached at least 9 x 10⁻⁹ Torr. Subsequent heating of the substrate was done in vacuo up to the desired final temperature. For oxides with varying indium oxide concentrations, each sample was scanned five times throughout different locations in order to ensure the integrity of the results. Gold substrates were sputtered cleaned in vacuum to ensure that their effective work functions were 5.1 eV and to provide for measurement of the Fermi level. Photoemission from the Au Fermi level occurred at 30.6 eV in our system for sputter-cleaned gold substrates. For analysis of the TiOPc/acceptor interfaces in Chapters 4 and 5, a UHV organic deposition system
attached to the Kratos spectrometer that allowed for depositions of organic thin-films and subsequent analysis were used. Thin-films were deposited (<Ås⁻¹) on gold substrates (Alfa-Aesar) that were polished and treated with piranha solution prior to the initiation of studies. Gold substrates were sputtered cleaned in vacuum to ensure that their effective work functions were 5.1 eV and to provide for measurement of the Fermi level. Photoemission from the Au Fermi level occurred at 31.9 eV in our system for sputter-cleaned gold substrates in Chapter 4 and at. Routine checks (once per day) were carried out throughout the experimental sessions in order to ensure that this energy did not change. For exploration of solvent-annealed TiOPc thin-films, after the initial deposition and UPS characterization, the thin-films were removed from vacuum into a nitrogen-filled glove bag and solvent-annealed as described above. Samples were then returned to vacuum, followed by subsequent UPS/XPS characterization and depositions.

2.2.8 Microscopy

Scanning electron microscopy was carried out in an FE-SEM (Hitachi – Model 4800) with a 15 kV accelerating voltage on as-prepared samples (i.e., no metallic over coating). The current maps and height images of the modified ITO were obtained using a Digital Instruments atomic force microscope (Veeco, Model Dimension 3100). For height images, silicon cantilevers (Mikromasch) were used in tapping mode. Images were obtained in ambient air at a scan rate of 0.5 Hz with image sizes of 2.5 x 2.5 µm. For current maps, the instrument was retrofitted with an extended TUNA module (Veeco) using boron-doped diamond tips (Veeco).
2.2.9 Visible Spectroscopy

Absorbance and transmission measurements were carried out in a UV/Visible spectrophotometer (Agilent, Model 8453) at 1 nm intervals with an integration time of 10 s. Absorbance measurements probed a varied with the type of experiment, but most experiments were acquired in a range between 400 and 1100 nm.
CHAPTER 3: MODIFICATION OF ITO WITH GOLD NANOPARTICLES

3.1 Introduction

Indium-tin oxide (ITO) electrodes modified with gold nanoparticles is the main topic of this chapter. Method development, mechanism of deposition, characterization, and effects on device behavior of small-molecule photovoltaics are covered. ITO has been described as a partially blocked electrode whose electroactive areas are randomly located throughout the surface region. These electrically blocked areas are suspected to be associated with tin-rich/oxygen deficient sites, resulting in highly localized electrical activity. This isolated activity results in sluggish electrode performance, as shown via probe molecule solution electrochemistry and solid state device tests (OLEDs, OPVs, OFETs). Any system that makes use of ITO would yield higher performance assuming these electroactive areas could be effectively maximized. For example, in OPVs this theoretically translates to a higher rate of hole collection during power generation. The primary goal of this work is the improvement of charge collection. Gold nanoparticles would serve as electrochemically wired systems that would preserve the electroactivity and transparency of the metal oxide, translating into higher performing devices. This would be evaluated by making small-molecule photovoltaics on these surfaces. Unlike most approaches which use spin casted gold nanoclusters, this method uses solution-grown metal species through several processing steps.
3.1.1. Conductive Surface Sites on ITO

Surface modifications of transparent conducting oxide (TCO) electrodes, such as indium-tin oxide (ITO), are often used to enhance performance in a variety of electronic devices.\textsuperscript{104,105} Unlike metal electrodes, even when thoroughly cleaned with detergents, activated with plasmas, UV-ozone, or strong acid/base treatments,\textsuperscript{60} ITO has been shown to remain “electrically blocked” on most sites on its surface. It has been recently shown that for some pretreatments, the surface can be as much as 90\% blocked.\textsuperscript{61} This blockage strongly impacts the electrochemical activity for small probe molecules and on its use as a hole-injecting or hole-harvesting contact for organic-based devices.\textsuperscript{106}

The most electrically active regions on ITO electrodes, with ca. 10\% concentrations of tin dopants, appear to be associated with Sn-rich sites, possibly due to SnO-like or Sn$_3$O$_4$-like inclusions.\textsuperscript{107} The most effective activation procedures appear to accentuate the near-surface concentration of these sites.\textsuperscript{60} Electrochemically deposited small molecules and polymers appear to nucleate first in the most electroactive regions, which have appeared to be localized along edge sites within the crystalline features on the ITO surface.\textsuperscript{105}

3.1.2. ITO Performance Improvements

Metal nanoparticles (NP) have been widely used to enhance the chemical and electrochemical reactivity of oxide systems; especially those comprised of the noble metal nanoparticles such as Au or Pt. Gold nanoparticle (Au-NP) surface modification has been used to enhance the optical properties of an oxide material,\textsuperscript{108} the catalytic
activity for certain gas phase chemical processes (e.g. oxidation of CO to CO$_2$), and the electrochemical properties of ITO within organic electronic devices. Recent studies have used spin casted gold nanoparticles as interfacial modifiers between the ITO electrode and small-molecules, donor-acceptor blends, and embedded into PEDOT:PSS buffer layers. Results from these studies displayed increases in photocurrent, fill factor, and open-circuit potential. The majority of the studies have credited the increase in photovoltaic device performance to a localized surface plasmon resonance (LSPR) effect, where the metal nanoparticles serve as propagators of electromagnetic waves that enhance the overall photoactivity of the device. Such effects are said to be playing a role when the overall Incident-Photon-Current-Efficiency (IPCE) is enhanced throughout the absorption profile.

3.1.2.1. Au-NPs on ITO

Most methods used for embedding Au-NPs into OPVs make use of spin cast gold nanocrystals. Although this approach employs a quick route for device fabrication, issues arise in interfacial studies due to difficulties in controlling film thickness and uniformity. It was therefore necessary to develop a method that allowed for more control of the processing. The controlled growth and modification of oxides via monolayer by monolayer would be an extremely useful approach. A common gold precursor [chloroauric acid (HAuCl$_4$)] is used to create a Au(OH)$_x$ sol film, in basic aqueous media, followed by annealing and other post-processing steps to achieve Au-NPs with controllable dimensions and distribution on the oxide surface (Figure 3.1).
The surface coverage, size, shape, chemical reactivity, and optical/electronic properties of these Au-NP assemblies appear to be strongly dependent upon the type of oxide used and the chemical/thermal processing steps required to create these particles. This method was used on ITO for the first time in this work leading to similar results seen in recent studies.\textsuperscript{114-116} The results obtained from developing this protocol for ITO is presented in the following sections.

3.2 Microscopy of Au-NP Modified ITO

3.2.1. Scanning Electron Microscopy (FE-SEM) of Modified ITO

In order to understand the deposition mechanism of Au-NPs on the surface of ITO, a series of substrates were created in which the deposition times were varied. Figure 3.2
shows micrographs for substrates with 15, 30, 45, and 60 minute deposition times after annealing and thorough ethanol washing. The nanoparticles deposit within narrow crevices and edge sites, where high electron densities exist due to dangling surface bonds and discontinuities within the small crystal domains. The average sizes of the particles were approximately 6 nm, with a range between 4 and 11 nm. As the time of deposition increases, both the surface density and size of the particles increased.

At 45 minutes deposition time, nanoparticle coalescence appears to progress via nearest neighbor interactions (Ostwald ripening). In addition, the location of nanoparticle deposition is no longer segregated to edge sites; instead, they begin to deposit on the larger crystal faces of the ITO. The results reveal certain properties about the deposition mechanism, the first of which is the effect of time on deposition. As it has been shown, the increase in deposition time has resulted in a greater number of particles being deposited on edge sites first and then on large ITO crystal faces, with the sizes of particles being affected simultaneously. In addition, as will be shown in the next section the electrical activity of ITO as a function of the features on the surface is directly related to where nanoparticles initially nucleate. The combination of these two conclusions leads to the possibility that the same surface chemical properties that control electrical conductivity also play a large role in the deposition mechanism.
3.2.2. Conductive Atomic Force Microscopy (C-AFM) of Modified ITO

The micrographs for C-AFM measurements of nanoparticles on ITO are shown in Figure 3.3. The surface of ITO after deposition of Au-NPs for 15 minutes exposure shows very small electrical activity relative to background. As the deposition time increases, so does the current through the Au-NPs. Due to the resolution limits of the instrument, individual particles could not be resolved; instead, a qualitative picture of overall conductivity is presented. The relationship between surface electrical conductivity and deposition time however is clearly demonstrated in these experimental results.
3.3 Photoelectron Spectroscopy Studies of Modified Surfaces

3.3.1 XPS/UPS of Au-NP Modified ITO Substrates

3.3.1.1 Variable Temperature XPS

A slightly yellowish film is deposited on the surface during Au-NP deposition on ITO from solution. Using the same conditions for deposition which were employed for the microscopy studies stated above (without the annealing step), a substrate was removed from solution and placed in the photoelectron spectrometer for analysis. Figure 3.4 shows the results obtained during heating of the substrate from 25 °C to 400 °C.
XPS analysis at room temperature shows that oxidized gold is the predominant surface species.\textsuperscript{120} The presence of metallic gold (Au\textsuperscript{0}) can also be seen at a lesser concentration. Gold oxide is known to be unstable at room temperature, therefore facile conversion to metallic gold is expected.\textsuperscript{82} Heating to 400 °C causes a progressive decrease of oxidized gold with a corresponding rise of the metallic species. The change seen in the oxidation state of the surface gold species is hypothesized to be due to the collapse of the gold oxide matrix formed during the deposition process into the formation of gold nanoparticles. Simultaneously, electrochemically-formed gold nanoparticles are thought to lay the foundation for most of the chemisorption that takes place on the oxide. Under high solution concentrations, physisorbed species are more prevalent than

![Figure 3.4: X-ray photoelectron spectroscopy results obtained from scanning the Au 4f region after successive heating of the Au-sol film. The initial results (25 °C) show the presence of oxidized gold (92 eV and 88 eV) with a small quantity of reduced gold (90 eV and 86 eV). As heating progresses, the collapsed of the gold oxide matrix can be seen while the increasing amount of reduced gold is also noted.](image-url)
chemisorbed ones. This situation can be assumed to be the same when a large quantity of the sol is deposited on the surface of the oxide, which is discussed below.

3.3.1.2. The Effect of ITO Sheet Resistance on Au-NP Formation

The initial deposition of Au-NPs along electron-rich edges and crevices leads to the suggestion that localized surface conductivity might be a contributing factor during initial film growth. To investigate further, sputter ITO films with varying ratios of indium and tin were prepared. Thin-films with varying concentrations of indium oxide and tin oxide [ratios of 90:10, 70:30, 50:50, 30:70, and 10:90 (In$_2$O$_3$/SnO$_2$) were deposited via pulsed DC magnetron (refer to Chapter 1, 2).

The transparency of ITO is understood to be dependent on the relative amount of oxygen vacancies and tin dopants that behave as shallow donors right below the conduction band. These dopants create a two electron donor level from the oxygen vacancy (assuming In$_2$O$_2$) and a one electron donor level via replacement of In$^{3+}$ cations with Sn$^{4+}$ throughout the matrix. Reduced tin oxide is also known to be active within the ITO lattice which unlike SnO$_2$ acts as a one-electron donor within the polycrystalline matrix. In these series of processing experiments, the conductivity of ITO as a function of indium oxide concentration was studied, with results shown in Figure 3.5.

The ordinate on the right-hand side of the graph shows the normalized sheet resistance, which ranged from 18 to 420K $\Omega/\square$ at initial exposure to atmosphere. Low concentrations of indium oxide showed high sheet resistance, with a drop in resistance
after the 50:50 In$_2$O$_3$:SnO$_2$ ratio. This can be attributed to the low quantity of donor states derived from the oxygen vacancies within the indium oxide.$^{50}$ Further increase in the indium oxide concentration leads to conductivities normally reported for commercial ITO ($\sim$ 15 $\Omega/\square$), which is due to a greater amount of vacancies and donor levels below the conduction band introduced via Sn$^{4+}$ cations.$^{50}$

These same substrates were then modified with Au-NP treatments and analyzed via XPS. The ratio of Au/[(Sn/In)] was determined by integrating the Au 4f$_{7/2}$ and 4f$_{5/2}$, Sn 3d$_{5/2}$, and In 3d$_{5/2}$ core-level lines, where indium was used as the internal standard. The results show that as the concentration of indium oxide and the concentration of increases, so does the amount of gold on the surface. These results show that surface conductivity of the oxide is an integral part of the deposition mechanism of Au-NPs.

Figure 3.5: Plot of the integrated peaks obtained from Au 4f, Sn 3d, and In 3d versus percent indium oxide in sputtered ITO (left) and sheet resistance of ITO (prior to modification) versus percent indium oxide within the same ITO (right). A proportionality between the amount of gold on the surface and sheet resistance of the ITO exists.
### 3.3.1.3. Au-NP Effect on the Work Function of Commercial ITO

The modification of ITO with Au-NPs is expected to provide some alteration in the electronic properties of the oxide surface, and ultimately devices. One measureable property is the ITO effective work function, which was measured via UV photoelectron spectroscopy. During the development of the protocols for Au-NP deposition, it was determined that the work function of ITO could be increased to that of pure gold (5.1 eV – Figure 3.6). Even under low solution concentrations (1.0 x 10^{-5} M) and longer deposition times (2.5 hours), which is expected to lead to sub-monolayer coverage, the work function could be tuned to 5.1 eV. These conditions were of particular interest since they represent the condition under which device substrates were created, discussed further below.

![Figure 3.6](image_url)

**Figure 3.6:** UV photoelectron spectroscopy data for control and modified ITO. Inset (A) shows the full spectra, where the modified substrate was created under the protocols used for device fabrication. Inset (B) shows a blowup of the low kinetic energy edge region, showing a shift in the edge due to Au-NP modification.
3.3.2. Visible Spectroscopy

3.3.2.1. Plasmonic Effects on Commercial ITO Substrates

Au-NPs located on the surface of modified ITO are expected to produce plasmonic effects. After annealing at 300 °C, a slightly purple hue can be seen on substrates that have been exposed to high concentrations of the deposition solution (Figure 3.7).

This hue is derived from the absorption of the gold nanoparticles. As it was noted in the series of timed experiments (section 3.2.1), the growth of Au-NPs is directly related to the amount of time that the substrates are exposed to the deposition solution. This is confirmed further by the results seen in Figure 3.8.

![Figure 3.7: Photograph of ITO exposed to a high concentration of the Au-NP modification protocol after annealing. The deep purple color is a consequence of the gold plasmon at 550 nm.](image)

The absorbance spectra of the substrates, which were sampled after the annealing process, before [Inset (A)] and after rinsing [Inset (B)] show the strong gold nanoparticle plasmonic absorption band at approximately 550 nm. Substrates prior to rinsing show
that as deposition time increases, so does the absorption, lending further credence to the hypothesis of physisorbed products being the major component during deposition. After rinsing however, the plasmonic band is significantly reduced due to the removal of the physisorbed species.

![Absorbance spectra of ITO substrates exposed to a high concentration solution of chloroauric acid. Inset (A) shows the absorbance prior to removal of the physisorbed product. Inset (B) shows the absorbance after the removal of physisorbed products.](image)

Figure 3.8: Absorbance spectra of ITO substrates exposed to a high concentration solution of chloroauric acid. Inset (A) shows the absorbance prior to removal of the physisorbed product. Inset (B) shows the absorbance after the removal of physisorbed products.

### 3.4 Gold Nanoparticle Nucleation and Deposition on ITO

#### 3.4.1 Sol-Gel and REDOX Type of Depositions

##### 3.4.1.1 Background from Water-Glass Chemistry

Metal oxide thin-films can be created via a series of techniques such as sputtering, CVD, PVD, etc. One of the simplest ways is through the *Sol-Gel* process. In this method, an alkoxy metal precursor is mixed together with water under acidic or basic conditions to generate hydroxide functionalized species, which ultimately react to form long-range metal oxide networks (Figure 3.9). One of the most studied systems in *Sol-Gel* chemistry is that of silicon-oxide. Tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate...
(TEOS) is mixed with water at a set ratio and either acid (HCl) or base (NaOH) to create the metal oxide network. Prior to the creation of the thin-film, a multi-stepped process must be followed to ensure quality film growth.\textsuperscript{119}

\begin{equation}
(RO)_{4n}M + 2H_2O & \rightarrow (RO)_{2n}M_{2} + 2ROH
\end{equation}

\textbf{Bifunctional Monomer Reactions}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.9.png}
\caption{Reactions displaying the Sol-Gel process. Inset (A) shows the base hydrolysis reaction in which alkoxy groups are immediately replaced by hydroxide components under the influence of water and catalyst. Inset (B) gives examples of the types of reactions that can occur with a bifunctionalized precursor, such as dimer pairs, chains, and ring structures. [Reproduced from reference 119]}
\end{figure}

The base catalyzed route is of specific interest to this work due to the close resemblance of conditions to that used in the deposition of Au-NPs. In this mechanism, the TEOS or TMOS is converted to a negatively charged pentacoordinated intermediate followed by the re-stabilization of the unit with a hydroxyl replacing one of the more
stable ethoxy or methoxy leaving groups (Figure 3.10). Following this reaction, a series of condensation reactions take place, leading to long-range metal oxide network formation that ultimately leads to a thin-film.

3.4.1.2. Possible Sol-Gel Mechanism and Support

The mechanism for the Sol-Gel route of gold nanoparticle deposition on indium-tin oxide begins with the conversion of ionized chlorinated gold to the hydroxylated species at a high pH (Figure 3.11). The presence of the hydroxylated species leads to the reaction leading to physisorbed Au-NPs, which can be removed as a fine purple powder through physical contact and/or sonication after annealing. Figure 3.12 provides an overview of the mechanism being proposed. In the sol-gel mechanism [(Inset (A)], surface hydroxyls are proposed to serve as nucleation sites for Au-NP formation. The isoelectric point of
ITO has been noted to be in the pH range of 6 to 8 however. Since these surface modifications are carried out under slightly higher pH, the rates of such reactions are predicted to be much less than those occurring amongst the species themselves. As the number of reactions increase over time, the metal oxide network (MOx) formed from the solution proliferates, leading to this route being the dominant mechanism for nanoparticle formation.

3.4.1.3. Possible Redox Mechanism and Support

```
\begin{align*}
\text{HAuCl}_4 & \leftrightarrow \text{H}^+ + \text{AuCl}_4^- & \log K = -1.00 \\
\text{AuCl}_4^- & \leftrightarrow \text{AuCl}_3 + \text{Cl}^- & \log K = -4.34 \\
\text{AuCl}_3 + 3\text{OH}^- & \leftrightarrow \text{Au(OH)}_3 + 3\text{Cl}^- & \log K = 22.50
\end{align*}
```

Figure 3.11: Equilibrium constants for the formation of the hydroxide terminated gold species. Rate constant information obtained from reference 78.

Unlike the sol-gel process, which results in physisorbed species that are easily removed via physical contact, the redox process is hypothesized to lead to chemisorbed species which are strongly affected by the length of deposition time. Inset (B) in Figure 3.12 shows the redox-based nanoparticle formation mechanism. Two conditions are considered to be required in order for this mechanism to take place: 1) movement of electron density from the near-surface region to the surface in order to provide the
necessary nucleation sites directly at the surface and 2) formation of a chemical bond between the surface and the oxidized gold species. The movement of electron density from the near-surface is hypothesized to be driven by the reduced/non-stoichiometric species of In$_2$O$_{3-x}$ and SnO-like or Sn$_3$O$_4$-like inclusions (X in Figure 3.12). The reduction of these species through simple bonding rearrangements within the crystal lattice (X’ in Figure 3.12) gives the necessary electron density required for chemical bond formation. Due to the lack of experimental data required in order to make a definitive conclusion, a generic formation mechanism is proposed, where the gold species can be anything from fully hydroxylated gold to the non-hydroxylated species. The prolific growth of Au-NPs in the initial minutes of deposition lends credence to this mechanism (seen in Figure 3.2) where a majority of the formation occurred along the highly electronically rich edge sites throughout the ITO surface.
Figure 3.12: Proposed mechanisms for gold-oxide matrix deposition (A) and nanoparticle (B) formation. Inset (A) shows the proposed route for the gold oxide matrix formation, where the mechanism is similar to a base-catalyzed sol-gel process. Inset (B) shows the proposed route for reduced gold formation, where the mechanism resembles that of typical redox process.
3.5 Effect of Bottom Contact Modification on Small-Molecule PVs

3.5.1 Current-Voltage Measurements of Au-NP Modified Devices

3.5.1.1 Donor-Specific Responses to Modified Bottom Contacts

Figure 3.13: Current-Voltage plots for the mixed phases of TiO\textsubscript{Pc} donor-based devices, where Inset (A) is the linear J/V plot and (B) is the semilog dark response. Devices were created on control (1) and modified (2) indium-tin oxide bottom contacts, where device architecture consisted of the following: ITO (150 nm), TiO\textsubscript{Pc} (20 nm), C\textsubscript{60} (40 nm), BCP (10 nm), and Al (100 nm). All substrates were air plasma cleaned and tested under AM 1.5G illumination conditions.

Devices constructed with TiO\textsubscript{Pc}\textsuperscript{84} and CuPc\textsuperscript{21} as donors and C\textsubscript{60} as the acceptor were chosen as test cases for studies using Au-NP modification of ITO. Figures 3.13 and 3.14 represent the average device performance seen for these systems with and without the Au-NPs. The mixed phases of TiO\textsubscript{Pc} show an increase of slightly lower than 50% in $J_{SC}$ with little change to $V_{OC}$ or $FF$ (Table 3.1).
Figure 3.14: Current-Voltage plots for Phase I TiO\textsubscript{P}c/C\textsubscript{60} and CuPc/C\textsubscript{60} devices. All devices were created on control and modified ITO electrodes. Inset (A) shows the linear plot for Phase I TiO\textsubscript{P}c/C\textsubscript{60} devices, while inset (B) displays the response seen for CuPc donor-based devices. Inset (C) and (D) show the semilog dark response for the TiO\textsubscript{P}c and CuPc donor-based devices.
<table>
<thead>
<tr>
<th>Donor Type</th>
<th>Device Type</th>
<th>$V_{oc}$[a]</th>
<th>$J_{sc}$[b]</th>
<th>FF[c]</th>
<th>$\eta$[d]</th>
<th>$J_0$[e]</th>
<th>$R_s$f</th>
<th>$R_p$[g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiOPc – AD[h]</td>
<td>Control</td>
<td>0.59</td>
<td>-4.5</td>
<td>0.41</td>
<td>1.1</td>
<td>3.0E-6</td>
<td>10.1</td>
<td>3.9E5</td>
</tr>
<tr>
<td>TiOPc – AD</td>
<td>Modified</td>
<td>0.62</td>
<td>-4.3</td>
<td>0.45</td>
<td>1.5</td>
<td>2.8E-6</td>
<td>56.3</td>
<td>2.4E5</td>
</tr>
<tr>
<td>TiOPc – PM[i]</td>
<td>Control</td>
<td>0.57</td>
<td>-7.38</td>
<td>0.50</td>
<td>2.1</td>
<td>1.5E-6</td>
<td>9.2</td>
<td>1.8E4</td>
</tr>
<tr>
<td>TiOPc – PM</td>
<td>Modified</td>
<td>0.54</td>
<td>-10.1</td>
<td>0.52</td>
<td>2.9</td>
<td>2.9E-6</td>
<td>4.5</td>
<td>3.3E3</td>
</tr>
<tr>
<td>CuPc – AD</td>
<td>Control</td>
<td>0.43</td>
<td>-5.2</td>
<td>0.57</td>
<td>1.3</td>
<td>5.1E-6</td>
<td>2.2</td>
<td>5.2E4</td>
</tr>
<tr>
<td>CuPc – AD</td>
<td>Modified</td>
<td>0.43</td>
<td>-4.8</td>
<td>0.56</td>
<td>1.2</td>
<td>3.1E-6</td>
<td>2.4</td>
<td>8.6E4</td>
</tr>
</tbody>
</table>

[a] = Open-circuit photopotential, V; [b] = Short-circuit current density, mA/cm$^2$; [c] = Fill factor, unitless; [d] = Efficiency, %; [e] Dark current density, mA/cm$^2$; [f] = Series resistance, Ω*cm$^2$; [g] = Parallel Resistance, Ω*cm$^2$; [h] = As-Deposited; [i] = Phase Mix

Table 3.1: Tabulated average results for devices tested with (Control) and without (Modified) gold nanoparticle surface modification.
Devices with as-deposited TiOPc exhibited an insignificant decrease in $J_{SC}$ and $FF$, while $V_{OC}$ increases from 0.58 V to 0.62 V; also not significant due to the average $V_{OC}$ values seen with TiOPc. CuPc-based devices demonstrated a decreases in $J_{SC}$, which were within experimental error for the measurement. There was little to no changes noted in $FF$ and $V_{OC}$. The variability in $J_{SC}$, $V_{OC}$, and $FF$ implies that the modification of the ITO electrode via Au-NPs is not leading to localized surface plasmon resonance (LSPR)\textsuperscript{112} and cannot be attributed to an increase in work function (Figure 3.6).\textsuperscript{111} These effects would be expected to increase both the overall $J_{SC}$ of any donor it comes into contact with and $V_{OC}$ across all three device platforms. Rather, it is behaving as a molecular-specific modification which may or may not necessarily lead to an increase in device performance.

The molecular-dependent behaviors seen in these series of studies show that oxide/donor interactions are significant factors in determining overall device performance. In the case of the mixed phases of TiOPc, $J_{SC}$ increased significantly when compared to the control devices. It has been shown (as discussed in detail in Chapter 4) that the Phase II component within this mixture of TiOPc has a much larger hole mobility when compared to its other phases as seen through molecular modeling calculations.\textsuperscript{96,123} This has been attributed to the increased overlap of the benzyl units on the periphery of the structure, which in turn stimulate the formation of CT excitons throughout (discussed below).\textsuperscript{124} As-deposited TiOPc did not exhibit changes in $J_{SC}$ and $V_{OC}$. The parallel resistance ($R_p$), which is used as a qualitative measure of thin-film quality (i.e. pin-holes), was not impacted significantly. For mixed phase TiOPc devices, the noted increase in $J_0$
coincided with a small decrease in $V_{oc}$ and increase in $R_p$. The increase in dark current is likely due to the increased surface area at the donor/acceptor interface, which in turn affects the rate of dark current injection into the system. The results seen for copper phthalocyanine used as a donor showed no significant changes in device behavior, like that for as-deposited TiOPc. It can be concluded that modification of the oxide bottom contact with Au-NPs will not necessarily always generate increases in device performance as first assumed. Instead, it is likely that the interactions between these systems are on a molecular level which is subject to change depending on specific conditions briefly explored above and studied further below.

### 3.5.1.2. Mixed Phase Device Studies

Incident-Photon-Current-Efficiency (IPCE) and absorbance measurements of a representative mixed phase TiOPc device are shown in Figure 3.15. Absorbance data shows a noticeable increase in absorption at approximately 840 nm for the modified ITO relative to the unmodified control. It has been shown that the transition near this wavelength is due to the Phase II polymorph of TiOPc, which is conclusive due to the initial phase transformation towards the Phase II polymorph during processing.\textsuperscript{99} Phase II TiOPc has been noted to have a higher hole mobility when compared to as-deposited TiOPc, and its charge-transfer exciton provides significantly higher photoactivity overall.\textsuperscript{96} IPCE measurements confirmed that the photocurrent was indeed higher within the near-IR, specifically at ca. 840 nm. However, integration of the IPCE over the spectrum of the lamp that was incident on these devices when tested (Appendix C)
showed that no gains would be made from this small change in response, where it was predicted that both devices would net -12.2 mA/cm². It can be concluded therefore that overall photoactivity of the devices on modified ITO cannot arise solely on the increased amount of Phase II TiOPc. Instead, chemical interactions that arise between TiOPc and the Au-NPs during the solvent-annealing process are possible causes of these noticeable changes in photocurrent collection. A potential mechanism is outlined below.

![Figure 3.15: Absorbance (A) and IPCE (B) measurements of TiOPc thin-films and devices with and without surface modification. Inset (A) shows the effect of surface modification on 20 nm of Phase mixed TiOPc on ITO, where the absorbance in the near-IR has increased. Inset (B) displays the averaged (n = 3) normalized IPCE for the control and modified devices, where the increase in the near-IR response is confirmed to be hypothetically derived from an increase in the Phase II quantity.](image)

3.5.2. A Model for the Molecule-Specific Response

3.5.2.1. *The Interactions of TiOPc and Pcs with Gold Surfaces*

TiOPc and other similar phthalocyanines have been investigated due to their molecular properties which include high electron mobilities and strong absorption in the visible portion of the electromagnetic spectrum. Many studies have focused solely on TiOPc and its structural packing properties during the deposition process. Fritz and co-workers deposited TiOPc submonolayers on single crystal gold which were then
monitored via Differential Reflectance Spectroscopy (DRS). Their results showed that TiOPc has very strong interactions with the substrate for the first two monolayers grown onto these surfaces. This was determined via the broad and unresolvable response in the near-IR. It was concluded that the formation of hybrid states could be rationalized based on the lack of coherence seen in the DRS spectra. Other Pcs on the surfaces of gold have also been investigated. Barrena et al. showed that phthalocyanines with different metal centers and peripheral modifications deposited on gold nanoparticles supported on a Si wafer would spontaneously template around the nanocrystal. Control of substrate temperature and nanoparticle size during these depositions could further influence how these Pcs would grow (mono or polycrystalline) and self-organize.

3.5.2.2. Explanation for the Increase in Photoacitivty

The results observed for OPVs using CuPc and TiOPc as donor layers show that the types of donor in which the Au-NP modified surfaces come into contact with are not the only factor governing performance. It is also the positioning of the molecule relative to the nanoparticle that impacts device behavior. The mixed phase TiOPc system showed significant differences when compared to the as-deposited, which can be explained by understanding the molecular level effects occurring during the solvent-annealing process. During the deposition of TiOPc at normal rates for this study (Chapter 2), the ability of TiOPc to order itself into its preferred position is relatively limited due to the high rate flux from the deposition source, therefore leading to a mixture of small-range crystal structures, known as the as-deposited phase. Saito and co-workers showed that this
type of phase exhibits no diffraction pattern as opposed to those that are seen for the higher order phases of TiOPc.\textsuperscript{102} The absorbance data in the literature for this phase is identical to that which is seen in these experiments.

Higher order crystal phases of TiOPc can be obtained via various methods, the easiest of which is to place a thin-film in an atmosphere saturated by solvent.\textsuperscript{96,98,126} Depending on the solvent and length of exposure, the higher order Phase I, II, or III is generated as discussed in Chapter 4. During this solvent-annealing, a rearrangement of the molecules into longer-range structures (nanometers) takes place. In addition, movement of molecules within the thin-films is likely occurring during this process.

It’s surmised that Au-NPs are behaving as catalytic centers for facile transformation into higher order TiOPc crystal phases during the annealing process. As mentioned above, a reactive relationship between TiOPc and gold surfaces has been shown to be present. However, it is not simply the creation of higher ordered polymorphs that generate the photoactive response and corresponding reduction in series resistance. The control and modified substrates showed no significant differences in photocurrent back-calculated from IPCE data. It can be concluded that solvent-annealing is causing the TiOPc to achieve a level of interaction with the Au-NPs that facilitates electron transfer at the oxide/organic interface. This facilitation leads to reduction in series resistance, therefore affecting the fill factor, and increases in photocurrent density leading to higher performing devices.
3.6 Summary and Conclusions

In this chapter, the modification of ITO substrates with Au-NPs has been explored. Characterization of these surfaces showed that the modification are strongly dependent on the concentration of the solution and the length of solution exposure. Based on scanning electron micrographs of substrates that were exposed to solution for short times, deposition of the nanoparticles was concentrated on electronically-rich sites on the surface of the oxide it was concluded that the majority of the deposition leads to physisorbed products, while the minority is governed by chemisorptions. The physisorption products are shown to derive from a sol-gel mechanism, which is based on a series of condensation reactions that leads to extended metal oxide networks. The chemisorbed products are hypothesized to be strongly affected by the sheet resistance of the oxide, which was confirmed via analysis of Au-NP deposition on ITO with varying conductivity.

The original premise was that modification of ITO with gold nanoparticles would increase the performance of small-molecule planar-heterojunction devices. This was based on the established idea that ITO is a partially blocked electrode whose most electroactive sites are blocked via surface contamination. It was proposed that after modification, such sites would become assessable due to the ability of gold to remain unreactive. The use of the modified substrates in photovoltaic devices showed that the improvement of performance is highly dependent on the type of donor system used and its level of interaction with the Au-NPs. While TiOPc and CuPc showed insignificant gains in all performance parameters (open-circuit photopotential, short-circuit current
density, fill factor, series and parallel resistance), the mixed phases of TiOPc showed improvements in photocurrent density and series resistance. A survey of the literature shows that there are strong interactions between TiOPc and gold surfaces, which can only be fully exploited when the molecule is given the opportunity to rearrange itself during the solvent-annealing process with respect to the gold nanoparticle.

These increases in performance led to further investigation using IPCE, which showed higher Phase II TiOPc activity in the near IR. However, these performance gains cannot be solely attributed to the higher ordered polymorph, but rather on the molecular-level interactions between the nanoparticles and TiOPc. It was shown that phthalocyanines deposited under conditions provided for molecular ordering (higher temperatures) will rearrange around nanoparticles of gold, leading to the possibility that the same situation is taking place under solvent-annealing. It is therefore expected that this enhancement is not specific to TiOPc, but to all of metal phthalocyanines provided they are given the chance to find their optimal energetic conformation. It can be concluded that the modification of ITO with Au-NPs does improve device performance, although this can only be realized by donors with specific interactions to the particles.
CHAPTER 4: TiOPc POLYMORPHS FOR DEVICE APPLICATIONS

4.1 Introduction

The focus of this chapter is on the study of the near-IR properties, texturing ability, and increase in charge mobilities of the higher ordered polymorphs of titanyl phthalocyanine for use in small-molecule photovoltaics. Titanyl phthalocyanine is known to have several crystallographic polymorphs whose texturing, absorption in the visible/near-IR, and hole mobilities vary. These crystallographic polymorphs can be generated via processing methods, of which solvent-annealing is one of the simplest. It is assumed that increases in the active surface area from texturing, the absorption into the near-IR, and the hole mobility would all translate into positive performance gains in small-molecule photovoltaic devices.

Device performance gains were expected in increased photogeneration and in the series resistance of the device, while a decrease in open-circuit photopotential was anticipated. The efficiency of photogeneration would be expected to increase due to the enhanced interfacial contact area between the TiOPc and the acceptor (C₆₀). The series resistance would be expected to decrease due to the increase in hole mobility of the higher ordered polymorphs relative to the as-deposited film. The open-circuit photopotential would be expected to decrease due to the pinhole density that would potentially increase as a function of texturing. When these effects are combined, the gains made in device efficiency would be expected to outweigh the negative impacts from using the higher ordered polymorphs for device applications.
4.1.1 Titanyl Phthalocyanine: Polymorphism and its Implications in OPVs

4.1.1.1 Exploitation of the Phases of TiOPc for Photovoltaic Applications

In Chapter 1, the solid state properties of titanyl phthalocyanine were described, the most important being the crystal polymorphs and its applications in OPVs. Figure 4.1 shows the absorbance spectra and crystal structures associated with the best characterized titanyl phthalocyanine polymorphs. Inset (A) shows the molecular model of TiOPc, while Inset (B) shows the absorbance spectra for thin-films of the four most studied polymorphs of TiOPc: as-deposited, Phase I (β-phase), Phase II (α-phase), and Phase III (γ-phase) TiOPc. Inset (C) and (D) show the crystal structure of the Phase I and II polymorphs.

Studies on the various phases of TiOPc (and other molecules like ClInPc\textsuperscript{127}) and the structural implications for PV applications was first reported by Tsuzuki and co-workers\textsuperscript{85}. They showed that there was a significantly higher photoactive response using Phase II compared to the as-deposited phase\textsuperscript{84}. Testing under monochromatic conditions near the Q-band of the phases, they found significantly higher short-circuit current densities ($J_{SC}$), while the open-circuit photopotential ($V_{oc}$), and fill factors (FF) remained the same. This increase was attributed to the high absorption coefficient and higher photoactivity of the molecule. They demonstrated that the properties of highly photoactive phases of pigments such as TiOPc could be exploited for use in planar-heterojunction OPVs.
The viability of TiOPc as a donor for photovoltaic devices was further studied by Brumbach et al.\textsuperscript{84} Using the as-deposited phase, they showed higher device performance is possible based on the larger $V_{OC}$ values obtained due to the higher ionization potential of TiOPc. Their analysis of the heterojunction between C$_{60}$ and TiOPc via UV-Photoelectron Spectroscopy (UPS) showed that a significant interfacial dipole was present. Further consideration to the properties of higher ordered TiOPc polymorphs in PV was given by Placencia et al., where it was shown that increased photocurrent could be obtained via nanotexturing.\textsuperscript{83} The central theme of this chapter is the physical source

Figure 4.1: (A) Space-filling model of titanyl phthalocyanine (TiOPc), where the oxo-titanium bond extends out of the plane, creating a strong intermolecular dipole. (B) UV-Visible spectra of four of the most studied polymorphs of TiOPc: the as-deposited and Phase I ($\beta$-phase) (which give nearly identical spectra), Phase II ($\alpha$-phase), and Phase III ($\gamma$-phase) TiOPc. X-ray crystal structures of the monoclinic Phase I (C – along the b axis) and the triclinic Phase II polymorph (D – along the b axis). The convex pairs and concave pairs are highlighted.
of this observed increase in photocurrent.

4.1.1.2 Processing Conditions for OPV Applications

One of the problems associated with trying to optimize a process for making planar-heterojunction OPVs is the limited thickness range of thin-films comprising the devices (ca. 20 nm for small-molecules). Processing steps, such as adding nanoparticles (Chapter 3)\textsuperscript{111} between the donor and oxide, or trying to create high surface areas can cause pinholes throughout the thin-film, leading to a lowering of the $V_{OC}$. Unlike bulk heterojunction systems, where interdigitization of the donor-acceptor system is possible due to the long exciton diffusion lengths associated with the polymeric/derivatized fullerenes, small-molecule systems composed of molecules such as phthalocyanines,\textsuperscript{83} squarines,\textsuperscript{129} and polyacenes\textsuperscript{130} possess relatively small exciton diffusion lengths, no larger than 20 nm at most.\textsuperscript{23} This prohibits the use of thicker ($x>50$nm) thin-films, which in turn limits the performance to relatively low efficiencies (ca. 5%). For titanyl phthalocyanine devices, a maximum thickness of 20 nm was reached before a quick drop-off in performance was seen during the optimization process (Figure 4.2). It is likely that exciton recombination, in addition to annihilation of carriers generated at the interface leads to decreasing performance.

As mentioned previously, titanyl phthalocyanine possesses the ability to re-arrange itself structurally on the molecular level, which in turn results in dramatic differences in the visible absorption profile,\textsuperscript{97} exciton diffusion lengths,\textsuperscript{96} and thin-film structure,\textsuperscript{98} all of which affect device performance. Clearly defined Phase I, Phase II, and Phase III
polymorphs result from deposition at higher temperatures on substrates whose surface free energy has been lowered by chemical modification with non-polar small-molecules, or through post-deposition solvent-annealing. Solvent-annealing of the as-deposited TiOPc provides a pathway for creation of the higher order polymorphs as well as texturing of the Pc film (confirmed for Phase II and III).

Figure 4.2: Plots of device parameters as a function of donor layer thickness. Thicknesses between 15 and 25 nm were investigated. A thickness of 20 nm was optimal for Phase II devices, showing higher performance in every parameter, with the exception of dark current density.

Figure 4.3 displays a series of Scanning Electron (SEM) micrographs, along with corresponding absorbance data that demonstrates the impact of solvent processing on 20 nm of TiOPc on indium-tin oxide (ITO). Solvent-annealing became the method of choice for creating the higher order polymorphs because of its ease and usefulness in processing large batches of samples quickly. Results show that chloroform was able to convert the as-deposited TiOPc to the Phase II more quickly when compared to acetone or ethanol. In addition, methanol was the only solvent that promoted the conversion from the as-deposited to the Phase III. All solvents roughened the surfaces to a higher degree when compared to the as-deposited thin-films (Figure 4.5).
Figure 4.3: Absorption [Inset (A), (C), (E), and (G)] and scanning electron micrographs [Inset (B), (D), (F), and (H)] of titanyl phthalocyanine (20 nm) deposited onto ITO surfaces exposed to methanol, acetone, ethanol, and chloroform. Ethanol, acetone, and chloroform seem to give the same polymorph, while methanol seems to give a different polymorph. All samples were solvent-annealed for 5 hours.
In this chapter, two polymorphs are studied in depth: the Phase II (α-TiOPc) and the Phase III (γ-TiOPc). Preliminary experiments did not yield working OPVs for the Phase III because film porosity lead to short-circuiting of the completed devices. Therefore, the processing was adjusted to only partially convert the as-deposited TiOPc film to Phase III, with the goal of obtaining the best performance (ca. 50-60% conversion was optimum). These hybrid films are referred to as “Phase III-like” for the rest of the study. As shown previously, severe roughening of the thin-films takes place during the processing. It can be expected that pinhole density throughout the thin-film would increase as a function of solvent-annealing time. This was monitored via the results obtained from testing a series of devices whose TiOPc thin-films were exposed to varying amounts of solvent-annealing times in chloroform (Figure 4.4).

Figure 4.4: Devices based on the TiOPc/C₆₀ heterojunction solvent-annealed under varying times with chloroform. The linear plots [Inset (A)] show large variations in short-circuit current density, with small variations in open-circuit photopotential. Semilog plots [Inset (B)] show large variations in dark current density. Small junction potentials at 0 Volts derive from stray light during the measurement. The best performance came from thin-films annealed for three hours, where reproducibility and device yield was used as the determinants for success.
4.2 Effect of Solvent-Annealing on TiOPc Thin-Films for OPV Applications

4.2.1 SEM Structural Studies

Titanyl phthalocyanine was deposited onto ITO surfaces that were pre-treated by air plasma. Following the deposition, the thin-films were analyzed as prepared or solvent-annealed with chloroform, or methanol. Figure 4.5 shows the SEM micrographs of the resultant TiOPc thin-films at a 45° take-off angle, where bare ITO [Inset (A)], 20 nm of as-deposited TiOPc [Inset (B)], 20 nm of Phase II [Inset (C)], and 20 nm of Phase III-like [Inset (D)] are displayed.

![SEM micrographs](image)

Figure 4.5: FE-SEM images (45° tilt) for (A) bare ITO, (B) 20 nm of as-deposited TiOPc on ITO, (C) TiOPc fully converted to Phase II on ITO, and 20 nm TiOPc partially converted to Phase III on ITO. The oxide showed an average rms roughness of 3.2 nm, while as-deposited, Phase II, and Phase III-like showed rms roughness values of 3.9, 5.5, and 7.5 respectively (Scale bar = 500 nm).
The micrograph obtained for bare ITO (RMS roughness = 3.2 nm) shows typical features seen for this oxide: large grains and associated sub-grain structures. As discussed in *Chapter 3*, the oxide can be thought of as a series of small crystal domains within a large matrix and is not completely amorphous. The ability of TiOPc to wet the oxide surface is evident after subsequent deposition of 20 nm on the air-plasma treated ITO (RMS roughness = 3.9 nm), the ability of TiOPc to wet the surface of the oxide is seen. With the exception of small aggregates seen throughout the micrograph, the molecule appears to conform to the oxide as evidence by the visibility of the ITO grain and sub-grain structures [Inset (B)]. After chloroform solvent-annealing [Inset (C)], severe roughening (RMS roughness = 5.5 nm) of the surface takes place. It is evident from these micrographs that surface reconstructions have occurred and emphases the strong role the solvent plays in lowering the activation energy for favorable molecule-to-molecule interaction. Crystallites ranging from 50 to 100+ nm can be seen throughout the micrograph; though it should be pointed out that they still are not small enough to be in the optimized range for efficient exciton dissociation. Solvent-annealing of TiOPc with methanol [Inset (D) – RMS roughness = 7.5 nm]) causes apparent de-wetting from the ITO surface, to the point where bare ITO is seen in the underlying background. This clearly differs from chloroform annealing, where the underlying ITO was at the very least covered with some overlayer. The mechanism for this is still unclear and is referred to future work.
4.2.2 UV/Vis Spectroscopy of TiOPc Phases

As discussed in Chapter 1, the visible spectrum of TiOPc is dependent on molecular environment. In transitioning from the solution phase, where TiOPc exists in dimer pairs,99 to the solid state, where molecules are tightly packed and constrained, degeneracy of the LUMO levels takes place. This degeneracy leads to the creation of two new separate LUMO levels, which are denoted as the LUMO+1 state (ca. 685 nm) and the LUMO state (ca. 720 nm) for the as-deposited phase. As the crystalline order increases with phase type (e.g. Phase II, etc.) so does the separation between these two states within the visible spectrum. As it has been reported by Saito and co-workers,102 Yamaguchi et al.,101,131 Mizuguchi et al.,99 and Nakai and co-workers100 the photogeneration efficiency for the LUMO state in either the Phase II or Phase III is higher relative to the LUMO+1. In an effort to understand the role of each LUMO state in the photogeneration process for the OPVs, the growth of a series of thin-film with phase gradients that would incorporate a certain fraction of a higher order phase within the total 20 nm of TiOPc was undertaken. For example, a 60% Phase X TiOPc thin-film (where X = II or III-like) results from deposition of 12 nm of as-deposited TiOPc, conversion to the Phase X polymorph, followed by deposition of another 8 nm of as-deposited TiOPc. To make devices for evaluation, this was followed by the remainder of the C_{60}/BCP/Al thin-films required for functionality.

Figure 4.6 shows the absorbance data for devices using as-deposited TiOPc going to either Phase II [Inset (A)] or Phase III-like [Inset (B)]. The percentage of active Phase X was varied from 0% to 100%, and the experimental thickness during the sequential
deposition process was 20 nm. As-deposited TiOPc shows typical characteristics associated with its phase, with similarities to the Phase I TiOPc. This phase can also be described as “amorphous” due to the inability to resolve structure in XRD measurements. This film demonstrates a strong absorption at 738 nm, which decreases in favor of a nearly equally sharp absorbance feature at ca. 854 nm after nearly full conversion to the Phase II polymorph. Note that even for the as-deposited thin-film, there is still appreciable absorbance up to 1050 nm.

Figure 4.6: Visible absorption spectroscopy of various mixes of as-deposited TiOPc and either Phase II [Inset (A)] or Phase III-like [Inset (B)]. As the progression from 0% to 100% progresses, the increase in the near-IR is obvious. Small quantities (20%) are enough to impact the absorption in the near-IR as much as that seen in the visible. Inset (B) does not show as much near-IR activity due to the lack of full phase change.

For ca. 60% conversion of these thin-films to the Phase II polymorph, the absorbance spectra suggest that there is still an appreciable concentration of the as-deposited species. Using methanol as the annealing solvent promotes the formation of the Phase III polymorph, although complete conversion is not seen to the same extent as for chloroform-annealed films in Figure 4.2. The near-IR absorbance feature is not as sharp
as for the Phase II polymorph and the presence of residual as-deposited absorbance features in the fully annealed thin-film is still appreciable.

4.3 Band-Edge Offset Studies of TiOPc/C₆₀ Heterojunctions via UV-PES

4.3.1 Band-Edge Offset Studies of Different Phases

4.3.1.1 As-Deposited /C₆₀ Band-Edge Offsets

The low and high kinetic energy photoemission spectra for a typical as-deposited TiOPc film along with the sequential growth of C₆₀ on top is shown in Figure 4.7. These spectra agree with what has been reported previously on this system. Deposition of TiOPc onto sputter cleaned gold surfaces (to a work function of 5.1 eV) shows a movement of the low-kinetic energy edge towards low-kinetic energy, resulting in a positive shift (away from vacuum level). Subsequent sequential growth of 72 angstroms

![Figure 4.7](image-url)

Figure 4.7: UV photoemission spectroscopy measurements of the as-deposited TiOPc, along with subsequent addition of C₆₀ onto that surface. Inset (A) shows the low kinetic energy edge, while Inset (B) shows the high kinetic energy edge, where the growth in the HOMO of C₆₀ is seen as a function of thickness.
of C\textsubscript{60} on the as-deposited TiOPc causes a very small shift in the low-kinetic energy region (0.1 eV). The high kinetic energy portion of the spectra shows little change until approximately 5 angstroms of C\textsubscript{60} are accumulated. Increasing amounts of C\textsubscript{60} eventually decreases the HOMO of TiOPc (30.3 eV), while strongly showing the C\textsubscript{60} HOMO at approximately 29.5 eV.

The band-edge offsets for the as-deposited TiOPc/C\textsubscript{60} heterojunction are shown in **Figure 4.8.** The energy value of the HOMO for as-deposited TiOPc agrees with values previously seen with C\textsubscript{60} by Placencia and Brumbach.\textsuperscript{82,83} Transport gaps for the molecules were not accessible by this technique, therefore, optical LUMOs were used as reference (not shown, discussed below). Although these are not strictly applicable due to the differences between transport LUMOs and optical LUMOs, they give a general idea of the energies related to true band-edge offsets.\textsuperscript{20}

![Figure 4.8: Band-edge offsets for as-deposited TiOPc/C\textsubscript{60} heterojunction. A small interface dipole is seen at the interface, with all other values relatively close (0.1 eV max difference) to previously acquired data.](image-url)
4.3.1.2 Phase II/C\textsubscript{60} Band-Edge Offsets

The UPS spectra for the Phase II TiOPc/ C\textsubscript{60} heterojunction and band-edge offsets are shown in Figure 4.9 and Figure 4.10. Unlike the as-deposited TiOPc, where C\textsubscript{60} was deposited over the surface immediately after deposition and spectral acquisition, the creation of the Phase II TiOPc required the extraction of the as-deposited thin-film from vacuum into a nitrogen filled glove bag where solvent-annealing occurred. The annealed film was subsequently reintroduced into the vacuum growth chamber and processed.

Figure 4.9: UV photoemission spectroscopy measurements of the Phase II TiOPc, along with subsequent addition of C60 onto that surface. Inset (A) shows the low kinetic energy edge, where a large shift is observed after solvent-annealing, while Inset (B) shows the high kinetic energy edge, where the growth in the HOMO of C60 is seen as a function of thickness.

The low kinetic energy portion of the spectra shows the same initial characteristics as the as-deposited TiOPc, followed by an increase in the kinetic energy for the photoemission [Inset (A)]. An effect similar to what is seen in this set of experiments was observed by Yamane and co-workers who deposited monolayers of TiOPc onto HOPG surfaces with subsequent heat treatment.\textsuperscript{132} They attributed the observed increase in kinetic energy to the surface orientation of the TiOPc (oxo-titanium bond facing away
from the surface) and the final state effects subsequent to photoemission. Although the specific orientation of the TiO\textsubscript{Pc} on the surface after solvent-annealing is unknown, it is proposed that both effects are likely contributing to the shifts seen here as well. Subsequent deposition of C\textsubscript{60} upon the solvent-annealed surface shows a small positive shift in kinetic energy (0.1 eV, away from vacuum level), which is opposite of that seen for the as-deposited system.

![Diagram](image)

Figure 4.10: Band-edge offsets for Phase II TiO\textsubscript{Pc}/C\textsubscript{60} heterojunction. A small interface dipole is seen at the interface, with all other values relatively close (0.1 eV max difference) to previously acquired data.

### 4.3.1.3 Phase III & Phase III-like/C\textsubscript{60} Band-Edge Offsets

Prior to determining the interfacial relationship between the Phase III-like and C\textsubscript{60} interface, a full Phase III TiO\textsubscript{Pc} thin-film was generated via a 5 hour solvent-anneal. The UPS spectrum for the Phase III TiO\textsubscript{Pc} system is shown in Figure 4.11. As expected, there are significant differences between the as-deposited system and the Phase III system.
with regards to work function, with the energy of the HOMO of both being the same (5.2 eV). Using UPS, the Phase III-like/C\textsubscript{60} interface was studied. Figure 4.12 shows the UPS spectra for the Phase III-like/ C\textsubscript{60} system as a function of C\textsubscript{60} film thickness. Figure 4.13 shows the band-edge offsets recorded for this interface.

Figure 4.11: FE-SEM images (45° tilt) for (A) bare ITO, (B) 20 nm of as-deposited TiOPc on ITO, (C) TiOPc fully converted to Phase II on ITO, and 20 nm TiOPc partially converted to Phase III on ITO. The oxide showed an average rms roughness of 3.2 nm, while as-deposited, Phase II, and Phase III-like showed rms roughness values of 3.9, 5.5, and 7.5 respectively (Scale bar = 500 nm).

Figure 4.12: UV photoemission spectroscopy measurements of the Phase III-like TiOPc, along with subsequent addition of C60 onto that surface. Inset (A) shows the low kinetic energy edge, where a small shift is observed after solvent-annealing, while Inset (B) shows the high kinetic energy edge, where the growth in the HOMO of C60 is seen as a function of thickness.
After solvent-annealing of the as-deposited film, a small (0.2 eV) shift is seen towards higher kinetic energy. This is significantly smaller than that for Phase II TiOPc. The growth of C\textsubscript{60} onto the surface of the Phase III-like polymorph causes further changes in the secondary kinetic energy edge similar to that of the as-deposited system. Due to the amount of as-deposited TiOPc expected to remain within the Phase III-like thin-film, this behavior was not surprising. Examination of the high kinetic energy portion of the spectra also shows that the as-deposited properties of the system are quite strong. Band-edge offsets of the Phase III-like/C\textsubscript{60} system are shown in Figure 4.13, where the only difference between the as-deposited system is in the slight differences in the HOMO energy and the slightly greater (ca. 0.1 eV larger) interface dipole.

Figure 4.13: Band-edge offsets for Phase III-like TiOPc/C\textsubscript{60} heterojunction. A small interface dipole is seen at the interface, with all other values relatively close (0.1 eV max difference) to previously acquired data.
4.3.2 Band-Edge Offset and Predictive Behavior

4.3.2.1 Open-Circuit Photopotential and Band-Edge Offsets

Determination of the highest and lowest occupied molecular orbitals is important in organic photovoltaics research. The relative energies of these levels in organic electronic devices such as OLEDs and OFETs have been linked to performance. In OPV studies, the values between these energies and the relationship to open-circuit photopotential have been investigated.\(^{34,35,133}\) The upper limit to the \(V_{OC}\) is proposed to be a function of the 
\[ E_{HOMO}^D - E_{LUMO}^A \] 
minus the energy required to dissociate the tightly bound electron-hole pair formed in organic systems (Section 1.4). Recently, others such as Postcavage et al.\(^{34}\) and Perez and co-workers\(^{35}\) have proposed additional factors that affect the \(V_{OC}\) such as the injection of dark carriers based on a Boltzmann-like relationship and structural components which affect the intermixing of atomic orbitals. Despite the numerous theories that have evolved, the energy difference between the highest and lowest occupied molecular orbitals is clearly important. In the sets of experiments discussed above, UPS was used as the main tool for characterizing the HOMO and corresponding work function of the organic semiconductors. Optical measurements were used to determine the LUMO of the, leading to the completion of the band-edge offset diagram. However, as has been shown by Zahn et al.\(^{20}\) and others,\(^{25}\) strict reliance on optical measurements for a value of the LUMO is incorrect due to the excess energy required for actual transport of the exciton across the thin-film. However, the use of optical data is practiced again in the next section and it is once again assumed to provide useful predictive behavior on the polymorph/C\(_{60}\) interfacial system.
4.3.2.2 TiOPc Polymorph/C\textsubscript{60} Offset Results and Predictions

The band-edge offset results presented above, along with the data that has been published on the relationship between \(V_{OC}\) and the \(E^{D}_{\text{HOMO}} - E^{A}_{\text{LUMO}}\) suggest that there will be no new behaviors in devices constructed using polymorph/C\textsubscript{60} interfaces. For each TiOPc/C\textsubscript{60} heterojunction, the \(E^{TiOPc}_{\text{HOMO}} - E^{C_{60}}_{\text{LUMO}}\) gap ranges from 1.1 eV to 1.3 eV. The observed \(V_{OC}\) for these heterojunctions is significantly smaller than these energy offsets. It has been shown that \(V_{OC}\) (comparable ClInPc/C\textsubscript{60} heterojunctions), can be as high as 0.8 volts, but these values are still 0.4 volts or more less than the maximum expected by these energy offsets.\textsuperscript{18}

4.4 Photovoltaic Devices Based on Solvent-Annealed TiOPc Thin-Films

4.4.1 \(J-V\) Performance of the Various Polymorphs of TiOPc

4.4.1.1 \(J-V\) Performance of As-Deposited TiOPc

The photovoltaic performance of as-deposited TiOPc is shown in Figure 4.14, with the linear [Inset (A)] and the semilog [Inset (B)] shown. This system typically exhibits an open-circuit photopotential (\(V_{OC}\)) between 0.60 – 0.65 V, short-circuit current densities (\(J_{SC}\)) at approximately 5 – 6 mA/cm\(^2\), fill factors (\(FF\)) ca. 0.5, and AM 1.5G efficiencies at approximately 2\%. Series resistances (\(R_s\)) typically range between 2 and 4 \(\Omega \times \text{cm}\(^2\)), with parallel resistances (\(R_p\)) usually between \(10^5\) and \(10^6\) \(\Omega \times \text{cm}\(^2\)). Reverse saturation currents (\(J_0\)) are typically as low as \(10^{6}\) s of mA/cm\(^2\). The performance seen for as-deposited TiOPc is similar to those seen for other phthalocyanine systems such as copper.
phthalocyanine and chloro-indium phthalocyanine, where the photocurrents are relatively low compared to bulk-heterojunction devices.\textsuperscript{18}

![Graph showing J-V measurements for the as-deposited TiOPc/C60 device.](image)

Figure 4.14: $J$-$V$ measurements for the as-deposited TiOPc/C60 device. The linear plot [Inset (A)] shows the typical response of the device, while the semilog plot [Inset (B)] displays similar behavior.

4.4.1.2 $J$-$V$ Performance of Phase Gradient TiOPc Layers

Devices based upon a mixtures of phases of TiOPc (as-deposited and Phase II or as-deposited and Phase III-like) were constructed and tested with results shown in Figure 4.15. Linear current-voltage curves for donor layers with varying degrees of conversion from as-deposited TiOPc films to either Phase II [Inset (A)] or Phase III-like [Inset (B)] polymorphs are shown, while Inset (C) and (D) show the semilog plots of the dark current. These sets of experiments performed to determine the relationship between the two optical transitions within TiOPc (LUMO and LUMO+1) and the carrier generating mechanism. By combining this data with that obtained from quantum efficiency measurements (see below), it is possible to distinguish the most photoactive transitions in the visible portion of the electromagnetic spectrum.
The resultant OPV device performance parameters are summarized in Table 4.1. For the as-deposited TiOPc thin-films, the photocurrent values and open-circuit photopotentials were typical of those seen in previous publications.\textsuperscript{18,83,84} The reverse saturation current, \( J_0 \), which helps to control \( V_{OC} \),\textsuperscript{24,25,34,35,135,136} was ca. 3.8 \( \times 10^{-8} \) mA/cm\(^2\), consistent with the formation of a uniform Pc film with low pinhole density and a large energetic barrier to dark charge injection into the C\textsubscript{60} phase. As the percentage of either the Phase II or Phase III-like polymorph increased within the films, the photocurrent yield increased, but only up to the point where ca. 60\% of the as-deposited TiOPc thin-film was converted to either the Phase II or Phase III-like polymorph. Above that conversion percentage, \( J_{SC} \) begins to decline slightly. It is proposed that at 60\% of Phase X, the combination of high surface area at the donor/acceptor interface and low pinhole density throughout the device is at its highest. The value of \( J_0 \) increases by nearly two orders of magnitude after solvent-annealing pre-treatment. This can be due to \( i) \) an increase in donor pinhole density and/or \( ii) \) an increase in probability for dark charge transfer to the acceptor phase as a result of the increase in interfacial contact area. Small decreases in \( V_{OC} \) were observed for Phase II or Phase III-like devices versus as-deposited TiOPc devices. The biggest changes were observed at about 40\% of Phase X; most likely due to a high density of pinholes throughout the thin-film. An exception was noted in the 20\% Phase III-like device, where an abnormally low photocurrent and open-circuit potential was observed.
Figure 4.15: J-V plots for OPVs with the configuration: ITO (150 nm)/TiOPc (20 nm)/C60 (40 nm)/BCP (10 nm)/Al (100 nm). Variable thicknesses (4 nm to 16 nm) of as-deposited TiOPc were deposited first, followed by solvent annealing, deposition of sufficient TiOPc to bring the total equivalent thickness to 20 nm, and then completion of the device. For example 60% Phase II or 60% Phase III-like results from conversion of 12 nm of as-deposited TiOPc to Phase X, followed by deposition of another 8 nm of as-deposited TiOPc. (A & B) Increases in $J_{SC}$ (>2x) are seen with increasing fraction of Phase II or Phase III-like polymorphs, where 60% Phase X showed the highest photocurrents. These increases in $J_{SC}$ are coupled with changes in both open-circuit potentials and dark-current values (C & D - see Table 4.1).
<table>
<thead>
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<th>Type</th>
<th>Phase (%)</th>
<th>$V_{OC}$[V][a]</th>
<th>$J_{SC}$[mA/cm$^2$][b]</th>
<th>$FF$[c]</th>
<th>$J_0$[mA/cm$^2$][d]</th>
<th>$J_{SC,AM1.5G}$ mA/cm$^2$[e]</th>
<th>$\eta_{AM1.5G}$[f]</th>
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<td>0.45</td>
<td>3.8E-8</td>
<td>-4.9</td>
<td>1.4</td>
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<td></td>
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<td>0.51</td>
<td>1.2E-6</td>
<td>-9.0</td>
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<td>0.49</td>
<td>4.6E-6</td>
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<td>3.5</td>
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<td></td>
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<td>-16.7</td>
<td>0.57</td>
<td>4.4E-6</td>
<td>-12.8</td>
<td>4.4</td>
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Table 4.1: Device performance parameters for the TiOPc/C$_{60}$ OPVs shown in Figure 3, as a function of the percentage of either Phase II or Phase III-like polymorph within the donor layer.
4.4.2 Quantum Efficiency Measurements

4.4.2.1 Incident-Photon-Current-Efficiency Measurements

I-V characterization of TiOPc devices showed that enhancements in photovoltaic properties could be achieved with a higher degree of ordering within the phthalocyanine film comprising the donor layer. Large increases in photocurrent and little to no loss in open-circuit photopotentials were observed for more ordered systems. In an effort to identify the photoactivity of the devices based on the incident wavelength IPCE characterization was initiated. Figure 4.16 shows the response of the devices as a function of % Phase X.

![Figure 4.16: Incident-Photon-Current-Efficiency measurements (IPCE) of several TiOPc devices with varying concentrations of higher ordered polymorphs embedded within. Inset (A) shows the as-deposited/Phase II TiOPc mix. Small quantities (20%) of the Phase II immediately increased the response all throughout the spectrum window, where it continues to grow thereafter. The as-deposited/Phase III-like [Inset (B)] cells show the same behavior, with the exception of the 20% device.](image)

As-deposited TiOPc devices show photoactive responses in the blue (400 – 550 nm) and in the red (600 – 800), which are attributable to the absorption by C₆₀ fullerenes, and
TiOPc respectively. The overall external quantum efficiency is lower relative to bulk-heterojunction and pentacene devices.\textsuperscript{6,137} As the Pc system becomes more ordered, there is a rapid increase in overall photocurrent and absorption in the near-IR (with the exception of 20\% Phase III-like). It has been observed that when the as-deposited system begins to shift from a disordered network of molecules (on a large scale) to a more orderly system, so does the energy difference between the two LUMO states.\textsuperscript{99} Unlike the response that was shown in the visible spectra of the mixed phase devices (\textit{Figure 4.6}), where the major absorption was occurring in one segment of the visible portion of the electromagnetic spectrum, these IPCE studies show that the photoactivity is being derived from both transitions (ca. 680 nm and 840 nm). Maximum IPCE values for the Phase II studies reached ca. 55\%, while they were lower for the Phase III-like at ca. 48\%.

\textbf{4.4.2.2 Absorbed-Photon-Current-Efficiency Measurements}

IPCE measurements conducted on TiOPc devices provided insight into the origin of the photocurrent as a function of wavelength. Absorbance measurements did not track the overall IPCE spectral response, thus showing that this characterization method does not distinguish between photons that create photocurrent and those that are absorbed but do not produce photocurrent. This is due either to low exciton diffusion lengths, energy loss (radiative and non-radiative), and/or low rate of photoinduced electron transfer (PIET). Absorbed-Photon-Current-Efficiency measurements (APCE) can be used to determine the number of absorbed photons that participate in photocurrent generation as a function
of wavelength. Figure 4.17 shows the APCE spectra for the mixed phase devices normalized to the highest APCE of the Phase II system.

![Figure 4.17: Absorbed-Photon-Current-Efficiency measurements (APCE) for devices with varying concentrations of higher ordered polymorphs embedded within. Like the IPCE response for the devices, the activity is shown to increase. The activity is shown to derive mostly from the ca. 680 nm region.](image)

This data confirms the trends seen in the IPCE data with respect to an increase in IPCE as a function of the increased percentage of higher ordered polymorphs. These APCE results suggest that the higher energy absorbance features near 650 nm lead to greater photocurrent yields than the features near 850-900 nm. Previous studies of excited state lifetimes and xerographic response where the TiOPc polymorph is used to photo-inject holes into a host polymer, have shown that this near-IR response (due to the formation of a charge-transfer (CT) excitonic state) is more photoelectrically active versus the absorbance feature centered around 650 nm. All of these studies suggest that the excitonic states formed at either 650 or 850 nm show 1-100 picosecond lifetimes; and both exhibit radiative and non-radiative decay channels which finally populate the lowest energy CT excitonic state. Estimating the energy of this state is
therefore a critical component of determining which polymorphic state is likely to generate more charge carriers in an OPV device.

4.4.3 Model for the Photocurrent Response of Textured TiOPc OPVs

4.4.3.1 Mixed Phase Systems

The experimental results obtained by varying the mixtures of TiOPc polymorphs within the active donor layer showed different characteristics with respect to device parameters. The performance was relatively poor with respect to as-deposited TiOPc OPV, such as 20% Phase III-like. Other mixtures demonstrated better performance. Based on previous studies using single crystals of higher order phthalocyanines with very high photoconductivities and higher hole mobilities, the photocurrent yield and efficiency of 100% Phase X was expected to be better than any other mixture. Referring to Table 4.1, two important points are evident; first, 40% Phase X shows a significantly higher dark current density \( J_0 \) and secondly, the 60% Phase X outperforms devices with higher concentrations of higher order polymorph.

For the films used in the 40% mixed-phase devices, it is important to understand that \( J_0 \) can be used as a qualitative measure of pinhole density and parallel resistance \( (R_P) \), throughout the donor layer, which in turn affects the open-circuit photopotential via (4.1):

\[
V_{OC} = \frac{nkT}{q} \ln \left( \frac{J_{SC}}{J_{SO}} \right) + \frac{\Delta E_{DA}}{2q} \quad (4.1)
\]
Where $-\Delta E_{DA}$ is the energetic barriers between the donor and acceptor and $q$ is the fundamental charge within the process.\textsuperscript{35} In addition, increases in the dark current density could arise from the probability for dark charge transfer to the acceptor phase changing as a function of the interfacial contact area. The combination of these two factors leads us to believe that at 40\% of Phase X, the contribution of having a high surface area between the donor and acceptor in addition to having the highest pinhole density leads to the highest dark current values. A visual representation of these effects is shown in Figure 4.18.

**Comparison of the 40 and 60 \% Phase X**

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</thead>
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<tr>
<td>Lower $V_{oc}$</td>
<td>Higher $V_{oc}$</td>
</tr>
<tr>
<td>Decreased Performance</td>
<td>Increased Performance</td>
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</table>

Figure 4.18: Hypothesized cross-section of the 40\% and 60\% Phase X used during device testing. The figure portrays some of the possible structural features of these surfaces. For example, the 40\% Phase X surface shows a high probability of high pinhole density, which in turn affects the device via higher dark carrier collection and lower open-circuit photopotential. The opposite is true with 60\%, where the performance is higher.

For the high performing devices with 60\% of Phase X, the results are similar to those with 40\% of Phase X, with the exception of pinhole density. Within this mixture of phases, the properties of the photoactive behavior of the higher ordered phases, along with the effects of a greater ratio between surface area and pinhole density is combined. The result is conditions that allow for higher photocurrent activity, with only a marginal
increase in dark current density (which in turn lessens the impact on the open-circuit photopotential) leading to optimal performance (Figure 4.15). Increasing amounts of higher order polymorphs beyond this point is likely to lead to a decrease in overall surface area, therefore reducing the amount of charges that can be extracted from the device.

4.4.3.2  Excitonic States in Photocurrent Generation

The data for mixed phase TiOPc devices show that there are likely two active HOMO-LUMO transitions. It was shown that the activity of these transitions do not follow literature expectations in which the red shifted transition would be significantly more active than that of the blue shifted transition.\textsuperscript{101,107,102} To explain this, it is useful to analyze the system in the context of the heterojunction architecture (shown in Figure 4.19) and not as an isolated system.

For as-deposited TiOPc, the peak of the Q-band absorbance at 738 nm creates an excitonic state with an energy offset with respect to the electron transport LUMO of C\textsubscript{60} (E\textsubscript{C60 LUMO}) of ca. 0.5 eV. For the two primary Q-band features for the Phase II polymorph of TiOPc, at 686 nm and 844 nm respectively, these energy offsets with respect to E\textsubscript{C60 LUMO} are 0.4 eV and 0.1 eV respectively. Estimates of the excess free energy needed to drive exciton dissociation and charge carrier formation at the Pc/C\textsubscript{60} interface have been made by Rand and coworkers,\textsuperscript{21} using a Marcus-like approach to predicting relative rates of charge transfer as a function of E\textsubscript{D LUMO} - E\textsubscript{A LUMO}. From this approach we would expect that the difference in charge generation efficiency for the excitonic features in
Phase II TiOPc films, at 686 nm and 844 nm, would be approximately a factor of 2x in favor of the higher energy absorption. This assumption is also coupled with the expectation that radiative and radiationless energy transfer from the higher energy excitonic state is slower than electron transfer to the acceptor, given the short lifetimes of these higher energy states. This leads to the conclusion that some energy transfer to the lower energy excitonic state, from which either luminescence or electron transfer events can occur, is taking place. Finally, the higher energy difference between the as-deposited phase and the acceptor must be explained. As shown by Saito and co-workers, the excitons in the as-deposited phase have a significantly higher Frenkel character than charge-transfer character. This would imply that there is a significantly higher energy cost associated with dissociating the exciton at the interface. It is likely that despite the fact that the as-deposited phase has a larger energy offset difference, the excitonic character prevents the production of a larger photocurrent relative to the higher order polymorphs.

An analysis of the APCE data for the fully converted Phase II TiOPc-based OPVs shows that the higher energy excitonic state is more efficient in photocurrent formation than the lower energy excitonic features by a factor of almost 2. This agrees with the predicted differences on the basis of the excess free energies available for the charge transfer event. The photocurrent yield clearly does not match the expected differences based on absorbance spectral changes alone, and there is some indication that excitonic features at ca. 900 nm and above have insufficient energy to form mobile charge carriers at the Pc/C₆₀ interface. Interestingly, when the electron acceptor was switched from C₆₀
to C\textsubscript{70} (Figure 4.20), for both the as-deposited and the Phase II TiOPc films, both maximum values in IPCE and APCE are increased by factors less than 2, and the APCE plots show nearly constant values from 650 – 900 nm. This suggests that the increased electron affinity of C\textsubscript{70} (ca. 0.1 – 0.2 eV higher than C\textsubscript{60}) makes the $E_{LUMO}^D - E_{LUMO}^A$ offset sufficient to produce photocurrent at all significant wavelengths, with larger increases seen in the near-IR transition of Phase II TiOPc. This confirms the higher photoactivity of the near-IR transition, which in our device architecture was being limited by the electron affinity of the acceptor.
Figure 4.20: Absorbance, Incident-Photon- and Absorbed photon-current efficiency (IPCE, APCE) measurements for Phase I/C\textsubscript{x} and Phase II/C\textsubscript{x} devices, where x = 60 or 70. (A&B) The absorbance spectra for both sets of data show no differences within the TiOPc region. (C)\textsubscript{70} absorption is significantly larger in both sets of data. (C & D) IPCE measurements show a large increase in current over the entire spectrum for both sets of data. (E & F) APCE measurements show that aside from an increase in the amount of photons that are converted to current, the LUMO + 1 optical transition in more active than its LUMO counterpart. As mentioned in the paper, this could be due to the increase in the band-edge offsets between the LUMO + 1 of the TiOPc and the C\textsubscript{60} transport LUMO.
4.5 Summary and Conclusions

In this chapter, the structure of the various polymorphs of TiOPc, their processing into thin-films, and their integration into organic photovoltaic devices was explored. It was initially thought that the higher ordered polymorphs of TiOPc would result in high performing devices. This is due to an expected higher amount of surface texturing, increased hole mobility, and extension of the absorbance into the near-IR. As exhibited by these phases of TiOPc, this behavior was confirmed. The growth of various higher order polymorphs (Phase II and Phase III) was made possible through the optimization of the solvent-annealing technique, which allowed for the control of high photoconducting polymorphs and manageable decreases in device performance. Ultraviolet Photoemission spectroscopy of the interface between the polymorphs and the C_{60} acceptor showed little differences exist in the HOMO of each polymorph, leading to the prediction of small changes in open-circuit photopotential and device operation. In order to study the effect of polymorph order, thin-films with variable fractions of as-deposited and either Phase II or Phase III-like were created. Visible absorption spectroscopy show significant absorbance in the near-IR with as low as 20% of either polymorph. Photovoltaic devices created with these films showed significant gains in performance, with peak values reached at 60% of Phase X, followed by a slight decrease thereafter. It is likely that at 60% of Phase X, the highest combination of surface area, the highest photoactive phase, and the lowest density of pinholes was achieved and as a result, the highest performing device. Quantum efficiency measurements (EQE and IQE) showed significant activity being derived from more ordered polymorphs in the near-IR. Interestingly, the optical
transition near 680 nm displayed the highest photoactivity. IQE measurements showed that the highest photoactivity was originating from this optical region, most likely due to the difficulty of dissociating the polaron pairs that originate in the near-IR. Using an acceptor with higher electron affinity showed that a significant amount of photocurrent from the near-IR is extracted due to the larger offset between the LUMO of the donor and the LUMO of the acceptor. This difference is known to control the rate of dissociation between polaronic pairs. It can be concluded that using the higher ordered polymorphs of TiOPc results in higher performance devices, giving a future direction for increasing device efficiencies for potential use in tandem devices.
CHAPTER 5: EFFECT OF DONOR/ACCEPTOR OVERLAP AT INTERFACE ON SMALL-MOLECULE PLANAR-HETEROJUNCTION DEVICES

5.1 The $V_{OC}$ in Small-Molecule Planar-Heterojunction Photovoltaics

The study of the co-facial overlap at the donor/acceptor at the molecular scale and its effect on device performance is the focus of this chapter. Molecules with structures and electronic properties different than C$_{60}$ are used in small-molecule planar heterojunction devices using TiOPc as the donor. As shown in Chapter 4, the effect of varying device architectures on the measured open-circuit photopotential was very pronounced. The observed effect on $V_{OC}$ for different mixtures of higher ordered polymorphs was proposed to be due to structural effects at the interfacial region. This is strong evidence that a systematic study and an understanding of the macro and molecular morphology of the interfacial region and its effect on $V_{OC}$ is critical. More specifically, it was proposed that the degree of co-facial overlap would have significant impact on device performance. This was due in part to the known effects that electronic coupling between the donor and acceptor would have on charge-generation, the open-circuit voltage, and dark carrier generation. This chapter focuses on the relationship between the open-circuit photopotential and the molecular organization at the interface studied using two perylene dyes as acceptors which have lower symmetry than C$_{60}$, and whose orientation at the interface can be parallel or perpendicular to the phthalocyanine substrate plane.
5.1.1 Analytical Expressions for \( V_{OC} \) in Small-Molecule PVs

In *Chapter 2*, a brief description of the properties of the open-circuit photopotential and its measurement in real devices was provided. When a device under illumination is held at \( V_{OC} \), the net photocurrent being measured from the system is zero.

Simultaneously, there is no net power that is being put into the system by the external source, where the recombination current is equal to the photocurrent that is being generated. In small-molecule planar-heterojunction photovoltaics, the \( V_{OC} \) is theoretically limited to the maximum of the difference between the LUMO of the acceptor and the HOMO of the donor (Figure 5.1). Potscavage and co-workers made the first attempt at describing this offset using pentacene/C\textsubscript{60} devices fabricated as the model platform.\textsuperscript{34}

Using the modified Shockley equation (5.1) to derive the open-circuit photopotential (5.2), they were able to develop an analytical expression for the open-circuit photopotential.
photopotential in terms of $E_{\text{HOMO}}^D$, $E_{\text{LUMO}}^A$, and the reverse saturation current. The terms are defined as: $J$ the current density, $R_S$ the series resistance, $R_P$ the parallel resistance, $J_0$ the dark current density, $V$ the voltage, $A$ the area of the cell, $n$ the ideality factor, $J_{\text{ph}}$ the photocurrent, $kT$ the thermal energy, $e$ the elementary charge, $J_{00}$ the prefactor, $-\phi B$ the effective barrier, $n'$ the adjusting ideality factor, and $-\Delta E_{\text{HL}}$ the effective barrier. The effective barrier is calculated from the difference between the HOMO of the donor and the LUMO of the acceptor.

These predictions were made possible by the observation that the dark current density could be modeled based on a thermally activated injection barrier with a Boltzmann-like distribution of states at the D/A interface (5.3). Based upon these analytical expressions, estimates on the open-circuit photopotential were made on pentacene/C$_{60}$, TiOPc/C$_{60}$, and CuPc/C$_{60}$ devices with close agreement to the experimental values.

$$J = \frac{1}{1 + R_S/R_P} \left[ J_0 \left\{ \exp \left( \frac{V - JR_s A}{n kT/e} \right) - 1 \right\} - \left( J_{\text{ph}} - \frac{V}{R_P A} \right) \right]$$ (5.1)

$$V_{\text{OC}} \approx n \frac{kT}{e} \ln \left( \frac{J_{\text{sc}}}{J_0} \right)$$ (5.2)

$$J_0 = J_{00} \exp \left( \frac{-\phi B}{kT} \right) = J_{00} \exp \left( \frac{-\Delta E_{\text{HL}}}{n kT} \right)$$ (5.3)

Further contributions to the understanding of the $V_{\text{OC}}$ were made by Perez and co-workers, where the physical interactions between the donor and acceptor were considered. They proposed the scaling of $V_{\text{OC}}$ is by a factor of $\Delta E_{\text{DA}}/2q$ rather than
$\Delta E_{DA}/q$, due to the thermal generation of an electron and hole. Thus was supported by their experimental results. In addition, they proposed that the prefactor ($J_{SO} - J_{00}$ in the Potscavge et al. publication) is not a constant due to differences in materials and molecular organization at the interface. They proposed a modified version of the equation (5.4):

$$V_{OC} = \frac{n k T}{q} \ln \left( \frac{I_{SC}}{J_{SO}} \right) + \frac{\Delta E_{DA}}{2q}$$

(5.4)

Where $J_{SO}$ is the prefactor determined experimentally that changes depending on the magnitude of physical overlap at the interface between the donor and acceptor, and the crystallinity of the donor material. This term also defined the theoretical dark current density ($J_S$) which was subsequently confirmed experimentally (5.5):

$$J_S = J_{SO} \exp \left( \frac{-\Delta E_{DA}}{2nkT} \right)$$

(5.5)

To test this theory, several donors were used in a planar-heterojunction configuration. The prefactor was calculated from the experimental data and showed good agreement with theoretical values. Donor systems that showed evidence for high crystallinity lead to high dark current density and therefore a decrease in the $V_{OC}$, while those that gave amorphous thin-films showed opposite behavior. The strongest contribution from the work of Perez and co-workers was showing that there is a strong relationship between the molecular interaction at the interface and the dark current density.

5.1.2 Approach Using Perylene Acceptors

Perez and co-workers have highlighted the importance of molecular interactions at the interface and its effect on the open-circuit photopotential.\textsuperscript{35} Their approach focused
on systematically increasing or decreasing the electronic coupling at the donor/acceptor interface by modifying the conjugation within the donor thin-film. In this work, the extent of donor/acceptor interactions is varied based on the orientation of acceptor molecules at the interface. Two perylene dyes (perylene-tetracarboxylic-bis-imide, PTCDA and perylenetetracarboxylic-dianhydride-N,N'-bis(butyl)imide, C₄-PTCDI), with different ionization potentials (IP), electron affinities (EA), and bulk structures with different cofacial interactions were used as electron acceptors. The different bulk structures (as demonstrated below) exhibited by these molecules are expected to yield different cofacial interactions with the underlining as-deposited TiOPc donor.

5.2 Characterization of Perylene Dye Acceptor

5.2.1 XRD Measurements

The orientation of PTCDA and C₄-PTCDI have shown to be different upon contact to smooth surfaces. XRD measurements for powder samples of these dyes are shown in Figure 5.2 and Figure 5.3. Results for 40 nm thick films grown on glass substrates for both perylenes are shown as insets. The pattern for PTCDA powder sample [Inset (A) in Figure 5.2] shows a clear diffraction peak at 27.88°, corresponding to the (102) plane in the α-PTCDA, as identified by Lovinger et al. Further, the presence of the peak indicates the growth of crystalline domains throughout the sample with the PTCDA molecules oriented parallel to the (102) plane. The distance between the flat lying molecules is on the order of 3.2 Å. This is the typical pattern associated with layer-by-
layer growth of PTCDA, which is shown in Inset (B). The thin-film of the perylene also shows this characteristic peak at 27.88 2θ.

The diffraction pattern for a powder sample of C₄-PTCDI is shown in Figure 5.3. The reflections near 6.5, 10.9, 19.4, and 25.4 2θ indicates the growth of the “Phase I” C₄-PTCDI, as noted by Mizuguchi et al.¹⁴⁸ The peak at approximately 6.5 2θ corresponds to the (020) plane, indicating a monoclinic unit cell where the molecules stand edge-on to the surface of the substrate [Inset (B)].
5.2.2 Visible Spectroscopy

The absorbance spectra of PTCDA and C₄-PTCDI are shown in Figure 5.4. Approximately 40 nm of each perylene was grown on glass for characterization. The absorbance maximum for both perylenes is centered about 500 nm, with the absorption of PTCDA about 0.4 A.U. higher than C₄-PTCDI at the very same maxima, most likely due to the loss of perylene(s) per unit volume as a function of the alkyl chains. From these measurements, optical bandgaps of approximately 2.2 eV and 2.1 eV were estimated for PTCDA and C₄-PTCDI, respectively.

![Figure 5.4](image)

Figure 5.4: Absorbance measurements of 40 nm of PTCDA and 40 nm of C₄-PTCDI deposited on glass substrates, where PTCDA has the highest absorbance of the two.
5.2.3 AFM Characterization

Observations on the surface morphology as a function of the perylene dye deposited over TiOPc were made via Atomic Force Microscopy (AFM). Inset (A) in Figure 5.5 shows an AFM image of 2 nm of PTCDA grown over 2 nm of TiOPc deposited on top of a Highly Ordered Pyrolytic Graphite (HOPG) substrate. Average roughness measurements of the image results in 1.0 nm rms. The observed uniformity is most likely due to the co-facial interactions between the TiOPc and the PTCDA. A typical micrograph for C4-PTCDI grown on TiOPc are shown in Figure 5.5, Inset (B). This sample exhibits significantly higher roughness and non-uniformity than the PTCDA/TiOPc system. As was shown by Schlettwein and co-workers, the modified perylene systems do not form layered structures as does PTCDA. Prior evidence suggests a growth pattern that is

![Atomic force micrographs of 2 nm of TiOPc deposited over 2 nm of PTCDA [Inset (A)] and 2 nm of TiOPc deposited over 2 nm of C4-PTCDI [Inset (B)] on HOPG substrates.](image)

edge-on to the substrate, causing preferential aggregation due to the lowering of
probability for $\pi$- $\pi$ interactions between the perylene and the Pc. These topographical observations agree with XRD measurements obtained above.

To further understand effects of the underlying TiOPc layer on the growth characteristics of the perylenes, PTCDA and C4-PTCDI were grown independently on HOPG substrates. Inset (A) in Figure 5.6 shows the height micrograph for PTCDA on HOPG. A smooth layer-by-layer growth results in roughness values averaging 0.8 nm rms. Inset (B) shows the growth of C4-PTCDI on HOPG. In contrast to PTCDA, this system does not appear to grow smooth orderly layers. The average roughness measurement was 1.7 nm rms. These results indicate that the growth mechanism of these perylenes are vastly different, which is the basis for the hypothesis that interfacial changes between each system and TiOPc might arise, leading to different device properties and interface energetics.

Figure 5.6: Height atomic force micrographs of PTCDA grown on an HOPG substrate [Inset (A)] and C4-PTCDI grown on an HOPG substrate.
5.3 Effect of Acceptor Type on the Device Performance

5.3.1 Current-Voltage Characterization

Previous chapters examined OPVs that used titanyl phthalocyanine (TiOPc) as the donor material. Device behavior was predictable, optimization parameters (i.e. thickness, surface pre-treatment of ITO) were known, and energetics properly characterized. This led to the decision to use TiOPc as the donor material within this new device architecture, employing alternative acceptors. Figure 5.7 shows the device performance of the TiOPc/PTCDA and TiOPc/C4-PTCDI systems, using 10 nm of bathocuproine (BCP), 100 nm of aluminum as top contacts, and pre-treated oxygen plasma etched ITO. These curves represent average device behavior observed over the course of the study with an active area of 0.125 cm$^2$. The PTCDA devices demonstrated a photocurrent response ($J_{SC}$) of approximately -4.5 mA/cm$^2$, an open-circuit photopotential ($V_{OC}$) of 0.32 V, a fill

![Figure 5.7: Current-Voltage curves for devices based on TiOPc/perylene heterojunctions. The device architecture consisted of ITO/TiOPc (18 nm)/Perylene dye (40 nm)/BCP (10 nm)/Al (100 nm). All devices tested under 65.5 mW/cm$^2$. Inset (A) shows the linear portion of the response in the dark and under illumination. Inset (B) shows the semilog version of the data, clearly showing the differences in dark current density between the two systems.](image)
factor (FF) of 0.4, and a dark current density ($J_0$) of $2.6 \times 10^{-5}$. For the C4-PTCDI device, the $J_{SC}$, $V_{OC}$, FF, $J_0$ were measured to be -2.9 mA/cm$^2$, 0.57 V, 0.42, $3.7 \times 10^{-7}$, respectively. The performance parameters for both devices are summarized in Table 5.1. For the PTCDA based devices, the photocurrent of the material is nearly double compared to C$_4$-PTCDI, but the $V_{OC}$ is lower. In addition, the dark current density is also opposite, while the same could be said for the series and parallel resistances. The series resistance values show that charges are more easily extracted from the device for PTCDA when compared to C4-PTCDI. C4-PTCDI devices show a higher value for parallel resistance, which can be attributed to the reduction in pinhole density throughout the thin-film or reduction of the dark electron transfer. The $J_{SC}$, $V_{OC}$, and, $J_0$ are discussed further below with regards to the relationship between the magnitude of these parameters and the energy offsets at the interface.

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<th>FF [c]</th>
<th>$\eta$ (%) [d]</th>
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<th>$R_p$ (Ohm $\cdot$ cm$^2$) [f]</th>
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<td>0.57</td>
<td>-2.9</td>
<td>0.42</td>
<td>1.1</td>
<td>5.1</td>
<td>7.6E+03</td>
<td>4.5E-07</td>
</tr>
</tbody>
</table>


Table 5.1: Performance values of the devices seen in Figure 5.7.

5.3.2 Optical Measurements

Visible spectroscopy and external quantum efficiency measurements were used to optically characterize the devices. Figure 5.8 shows the absorbance [Inset (A)] and IPCE
[Inset (B)] of the TiOPc/PTCDA and C₄-PTCDI devices respectively. The measurements show significantly higher absorbance and photocurrents for the device using PTCDA, due to the presumed higher co-facial overlap at the interface. In addition, the absorbance at ca. 730 nm resembles that of as-deposited TiOPc, as seen in Chapter 4.

The results of the external quantum efficiency measurements indicate overall lower efficiencies when compared to devices that make use of C₆₀ as the acceptor (Chapter 4). In addition to the change in photoactive response when going from the modified to the un-modified perylene dye in the 400 – 600 nm region, the response also changes significantly between the 600 – 850 nm region due to the part of the photocurrent generating mechanism that is dependent on the ability of the acceptor to extract charge. The end-result is that any improvement in charge-collection that is made with respect to either the donor or acceptor will lead to overall increases in device performance.

Figure 5.8: Optical response data for the devices based on the TiOPc/Perylene system. Inset (A) shows the absorbance of the entire device without aluminum, where the absorption between 400 – 600 nm can be assigned to the perylenes, while that between 650 and 850 nm is that of TiOPc. Inset (B) shows the IPCE of the devices with a maximum EQE of 27% for the PTCDA-based devices.
5.4 UV Photoemission Spectroscopy (UPS) of TiOPc/Perylene Interfaces

5.4.1 Spectra of TiOPc/Perylene Interfaces

Photovoltaic devices created within these studies consisted of employed an architecture in which the TiOPc was deposited on the ITO, followed by the perylene dye. It is observed that the sequence of film deposition yields different results via UPS with respect to interface dipoles. In the investigations into the energetics of this interface, the same deposition sequence was used for all samples. Deposition rate has not shown itself to be a factor in film analysis and device performance for this system.

![UV photoemission spectra of PTCDA deposited over a thin-film (ca. 20 nm) of TiOPc.](image)

Figure 5.9: UV photoemission spectra of PTCDA deposited over a thin-film (ca. 20 nm) of TiOPc.

UPS spectra for thin-films of PTCDA grown on TiOPc are shown in Figure 5.9. Inset (A) shows the secondary kinetic energy region (SKE) while Inset (B) shows the high kinetic energy region (HKE). Progressing from the bare gold to the TiOPc overlayer, a shift of approximately 0.7 eV in the SKE region is seen (1 to 2), with the HOMO of TiOPc clearly seen in the HKE (2). The 5.2 eV energy for the HOMO of TiOPc agrees with previously measured values. Subsequent addition of PTCDA onto the as-
deposited phase of TiOPc shows the HOMO of PTCDA growing into the HKE, while total shift in the SKE is measured to be approximately 0.3 eV. TiOPc/C₄-PTCDI interfaces were investigated in the same manner as the TiOPc/PTCDA system and shown in Figure 5.10.

![UV photoemission spectra of C4-PTCDI deposited over a thin-film (ca. 20 nm) of TiOPc.](image)

Figure 5.10: UV photoemission spectra of C4-PTCDI deposited over a thin-film (ca. 20 nm) of TiOPc.

### 5.4.2 Band-Edge Offsets

Band-edges offsets derived from UPS measurements for the TiOPc/PTCDA and TiOPc/C₄-PTCDI interfaces are shown in Figure 5.11. Due to experimental limitations, optical LUMO values were obtained as opposed to the transport LUMOs. The TiOPc/PTCDA band-edge offsets show that the HOMO for TiOPc is 5.2 eV with respect to the sample vacuum level. Its optical bandgap is approximately 1.7 eV, resulting in a calculated optical LUMO of about 3.5 eV with respect to the sample vacuum level. Upon the growth of ca. 19 nm of PTCDA, the formation of a significant interface dipole of 0.3 eV was observed. For the TiOPc/C₄-PTCDI, the interface dipole of 0.1 eV is
within the experimental measurement error (0.1 eV). Taking the difference in LUMO energies between the TiOPc and the perylene dyes gives $E_{\text{LUMO}}^{\text{TiOPc}} - E_{\text{LUMO}}^{\text{PTCDA}} = 0.9$ eV and $E_{\text{LUMO}}^{\text{TiOPc}} - E_{\text{LUMO}}^{\text{C4-PTCDI}} = 0.4$ eV. Alloway et al. previously showed that these differences are seen with trivalent phthalocyanines on PTCDA; however, it was noted that negligible interface dipoles were observed with C₄-PTCDI. They proposed that the co-facial contact between these molecules determines the magnitude of the interface dipole. It is likely that the system examined in this work is exhibiting similar properties.

![Band-edge offsets](image)

**Figure 5.11:** Band-edge offsets for the TiOPc/PTCDA [Inset (A)] and the TiOPc/C₄-PTCDI [Inset (B)] heterojunctions, where a significant interface dipole was noted for the perylene where it was expected that there is a significantly higher amount of co-facial contact to the donor system, while a negligible quantity was seen for the other perylene system.

### 5.5 Co-Facial Overlap at the D/A Interface and its Effects on Device Operation

In summary, there are two major points that arise from the data in this chapter. The first concerns the parameters obtained from devices, while the other relates to results obtained from the heterojunction studies by UPS. The device data shows that depending on the perylene dye used, photovoltage and photocurrent density are seen to be inversely proportional. Devices made with PTCDA yielded low open-circuit photopotentials and
high photocurrent densities, while C4-PTCDI based devices exhibited opposite behavior. UPS measurements showed that there are differences in the interface dipole between the two systems.

By interpreting this data, inferences can be drawn on the effects of co-facial overlap. It is known that the degree of co-facial overlap at the donor-acceptor interface will critically affect the device performance. Lemaur and co-workers explored the role of molecular dimensionality at the D/A interface and its effects on exciton dissociation and charge recombination. Due to the electron-transfer nature of these processes, Lemaur and co-workers proposed using a Marcus theory approach to analyze how these rates would change as a function of dimensionality. H2Pc and PTCDI were used as the model systems, where the electronic coupling parameter was monitored. Their results showed that the rates of exciton dissociation and recombination are adversely affected by the extent of spatial overlap between the wave functions of the molecules. The results from their work support the conclusion that overlap at the D/A interface is a critical component in determining the rates of charge generation.

The band-edge offsets between these two systems show that the magnitude of changes in the open-circuit photovoltage and photocurrent between the two systems can also be attributed to their electronic properties. A combination of these properties and the properties attributed to the co-faciality gives a more realistic working model to explain device behavior. The degree of co-facial overlap explains the difference in dark current density between the two systems. Perez and co-workers showed that donor systems with a high degree of crystallinity led to higher dark current densities. This was attributed to
the inability of disordered materials to participate in dark electron transfers as easily as those that form ordered systems. The XRD data obtained for the two perylene systems showed that crystallinity is high in both systems. This leads to the conclusion that there is a definite co-facial overlap contribution taking place at the interface that is affecting $J_0$, where C4-PTCDI exhibits lower dark current density when compared to PTCDA. This leads to the model proposed in Figure 5.12 for the interface on a small scale.

![Figure 5.12: Proposed heterojunctions for the TiOPc/PTCDA system [Inset (A)] and the TiOPc/C4-PTCDI system [Inset (B)].](image)

5.6 Summary and Conclusion

The studies presented in this chapter have focused on the attempt to understand the role of co-facial contact between the donor and the acceptor on the operation of small-molecule planar-heterojunction photovoltaics. It was proposed that the degree of co-facial overlap would lead to different results with respect to photocurrent generation, the open-circuit photovoltage, and dark current generation. The use of PTCDA and C4-PTCDI as electron acceptor probe molecules in research grade devices was investigated. The initial results showed that differences did exist in all performance parameters, with C4-PTCDI
showing the largest photovoltage, lowest current densities, and lowest dark current densities. The opposite behavior for every device parameter was noticed for PTCDA. UPS characterization of the interface showed that these differences could be, in part, attributed to interface energetics as well. The role of the degree of co-facial overlap could not definitively be quantified. The differences in dark current density, however, was attributed to the degree of co-facial overlap in agreement with previously reported data on the effect of crystallinity on the dark current density. These studies show that molecular architectures are critical in determining device operation and suggest future efforts towards the development of molecular systems with specific requirements to control specific operational parameters.
CHAPTER 6: CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusions

During the initiation of the research presented above, the state of the OPV literature was in different stages of development with respect to the three areas covered above; broadly described as 1) TCO surface modification, 2) electron donor texturing, and 3) molecular effects at the interface on device operation. The \emph{TCO surface modification} literature on OPVs was progressing quickly, with researchers identifying key problems preventing the contact from performing at its best.\cite{48} The \emph{electron donor texturing} literature was mildly developed, with attempts mainly from the Forrest group leading to marginal improvements.\cite{44,150} The \emph{molecular effects at the interface on device operation} literature was non-existent, with developments only a short time after the results in this dissertation were obtained.\cite{34,35}

This dissertation helped to shed light and potentially advanced the understanding within the three areas mentioned. In the \emph{TCO surface modification} area, the deposition of Au-NPs has given an additional route for improving device performance in small-molecule photovoltaics. Despite the impracticality of using gold, it provides evidence that the performance of transparent conducting oxides can be improved upon. In addition, it provides interesting problems that are worthwhile investigating that can have applications in other areas of science.

The \emph{electron donor texturing} research area was most impacted by the research presented above. The previous work by Forrest and co-workers showed that there was potential for improving device performance based on texturing of the donor. However,
their work was plagued by donor systems with no record of texturing and high photoactivity. The use of TiOPc, and the subsequent processing that went along with it, showed that high improvements in device performance could be made. As-deposited TiOPc cells showed that their performance was limited to ca. 1.5%. After texturing and change to the more photoactive phase, the efficiency was nearly 5% under AM 1.5G conditions. Although devices based on these systems will never reach market, tandem-based devices and other potential technologies can make use of this process due to the high photoactive response of the system in the near-IR.

The molecular effects at the interface on device operation is predicted to only certify the result that have been observed by Perez and co-workers, where interactions at the donor/acceptor interface were shown to severely impact on device operation. The work presented above was inconclusive in determining the full effect of molecular overlap due to the convoluted parameters between acceptor orientation and electronic parameters (LUMOs). However, concrete evidence was lent to the effect of molecular orientation on the dark current density. Whether this will lead to significant impacts on the literature is uncertain and will only be determined by the extent of development of OPV technology and its success.

### 6.2 Future Directions

The current state of small-molecule planar-heterojunction photovoltaics shows that interfaces are still playing a major role in the development of this technology. Currently, heavy focus is being placed on transition metal oxides and how they increase
overall device performance.\textsuperscript{27,151-155} Many systems like nickel oxide, molybdenum oxide, and others are being studied as alternatives to interlayer systems like PEDOT:PSS and small-molecule modifiers.\textsuperscript{6,59} Whatever system arises when the technology is commercialized on an industrial scale, these PV systems will never be fully optimized until the molecular-level aspects of the oxide/organic, metal/organic, and/or oxide (or metal)/interlayer/organic are understood. As survey of the literature has indicated, research focus has been on discovering materials whose bulk properties (e.g. optical transmission, energy levels, processability, etc.) best “fits” in between the oxide and organic material, while ignoring the molecular level interactions on the nanometer scale. These molecular level interactions have been shown by Alex Veneman,\textsuperscript{156} Gordon MacDonald,\textsuperscript{157} and partially this work to be large determinants in device performance. The studies in this dissertation, which reveal how molecular structure plays a significant role in determining device performance and how interactions between organic systems and oxides can alter device performance, leads to the recommendation for some future directions.

6.2.1. Oxide Modification via Cost-Effective Metals

The inability to maintain the native electrical properties of an oxide exposed to atmosphere pristine has been shown. Even after pre-treatments, the oxide has been shown to remain partially blocked.\textsuperscript{48} The studies presented in Chapter 3 showed that Au-NP modification helped to increase performance, based upon the hypothesis that the electrical properties of the oxide had been partially preserved, along with molecular-
specific interactions at the interface. The use of gold as the metal species however, renders this route useless. Therefore, discoveries of new modification protocols using alternative metal species should be pursued.

The mechanism for modification of these metal oxides involves straightforward sol-gel chemistry, where some weak leaving group is replaced by a hydroxide under basic conditions. Many metals are subject to the same mechanism, leading to the potential of creating a variety of metal nanoparticles that could potentially lead to the same improvements with a fraction of the costs relative to gold. Much research will have to be conducted in order to make this viable due to the differing of chemistries. However, assuming this can be overcome, the potential will not only affect the OPV field, but many others as well.

6.2.2. Rapid Surface Roughening Processing

Solvent-annealing of titanyl phthalocyanine thin-films showed that surface roughening was possible via exposure to high vapor pressure solvents. This was a clear advantage with respect to the high surface area increase at the donor/acceptor interface. The problem with this approach concerns the amount of time required to create these surfaces (3 hours total). Since there is a possibility for this method to be employed with other systems and/or industrial applications, a faster processing step is needed. High pressure flash solvent-annealing (HPFSA) is one route that could be employed. During optimization of the solvent-annealing process developed in this dissertation, it was noticed that direct overhead exposure of the TiOPc thin-film to the solvent led to the
conversion of high ordered polymorphs in a matter of minutes (ca. 10 mins.). This was spectroscopically confirmed as the Q-band shifted towards the NIR via UV/Vis. It was also noticed that long-term exposure led to fragmentation of the thin-film into large aggregates. Therefore, HPFSA is hypothesized to lead to the formation of highly photoactive phthalocyanines (or other species with the same response), in addition to severely roughened surfaces. This process could be achieved by pressurizing and heating a chamber with the desired solvent to the proper levels, along with the substrate inside. The potential for creating these surfaces can potentially lead to even higher surface areas, leading to the use of even thicker thin-films. The combination of these two factors would translate into higher device efficiencies.
APPENDIX A: DETERMINATION OF LIGHT SOURCE POWER FOR PHOTOVOLTAIC DEVICE TESTING

A.1 Determination of Spectral Output

Ideally, the light source used for photovoltaic light testing should be as close as possible with respect to spectral irradiance to the standard AM 1.5G. The lamp that matches this spectral irradiance the closes is the xenon arc lamp. Figure A.1 shows the spectrum of the AM 1.5G [Inset (A)] and a xenon arc lamp with and without the AM 1.5G filter [Inset (B)].

Figure A.1: Inset (A) shows the standard AM 1.5G spectrum used for solar cell performance evaluation in the national labs such a NREL. Inset (B) shows spectra for a standard 300 W Xe arc lamp with and without the AM 1.5G optical filter.

Companies like Newport Corporation sell the filter required to match this standard as close as possible. Assuming that the lamp being used is a xenon arc lamp, we begin the process of light source calibration by assembling all components as shown below (Figure A.2). The Figure shows the diagram with all necessary focusing optics, which should match the F/# of the monochromator, along with the lock-in amplification system, iris’, and photodetector. Typically, lock-in amplification is not required. However, xenon
sources contain a significant amount of signal spikes in the near-IR. These effects result in unreliable data being obtained if this is not compensated for. With respect to the photodetector, it should have good responsivity in the visible/near-IR region. Figure A.3 shows the responsivity of a typical Si photodiode from Newport.

![Block diagram of the instrumental setup required for lamp calibration.](image)

We begin the experiment by acquiring the spectrum of the lamp, which is a function of the current measured at the detector. Good analytical practice calls for at least three measurements in order to ensure reliability. Averaging of these three acquisitions leads to Inset (A) in Figure A.4. Multiplying the responsivity of the detector with the spectrum of the lamp, followed by dividing the power by the incident area leads to the average irradiance [Figure A.4, Inset (B)].

Take note that the grating being used within the monochromator has an efficiency of dispersion per unit wavelength. These efficiency curves can be obtained from the manufacturer, which are typically given as P-Plane (TE polarized light) and S-Plane (TM polarized light). Inset (A) in Figure A.5 shows the efficiency curves for a 350 nm blazed
grating from Newport. The average of these two curves is taken, shown in Figure A.5, Inset (B). Knowing that the light prior to entering the monochromator was not that which is seen in Figure A.4, we correct this spectrum by setting up a proportionality by solving for 100% efficiency. This leads to the corrected spectrum seen in Figure A.6. Now that you have the spectrum, assuming that there is no uneven loss of transmission while the light travels through the focusing lens’ prior to it entering the monochromator, you can be assured that this is the real nature of the light.

For the sake of simulating standard conditions, an AM 1.5G filter is placed in front of the housing assembly. Therefore, the spectrum of this filter [Inset (A) in Figure A.7] is obtained and multiplied across the power spectrum to give Inset (B) in Figure A.7. This corrected spectrum now allows for integration of Figure A.7, Inset (B) in order to obtain the total power [Figure A.8, Inset (A)]. In this particular case, the integration resulted in a total power of 0.052 W/cm². With this value, we can now find the correction factor needed in order to give the desired power. The AM 1.5G calls for ~0.1 W/cm² as the
power incident on the device during testing. Therefore, a proportionality could be setup where \([(0.052 \text{ W/cm}^2)/(0.1 \text{ W/cm}^2)]\) is set equal to \((1/x)\), where \(x\) is the factor that will be multiplied across the entire spectrum in Figure A.7, Inset (B). Solving for this factor gives a value of 1.92, whose total power after integration is equal to 0.1 W/cm\(^2\) [Figure A.8, Inset (B)].

Now that you have the spectrum at 100 mW/cm\(^2\), you would need to see what the response would be for the detector used during the calibration procedure prior to PV testing. In this case, we use a silicon photodiode, like the one used for obtaining the lamp spectrum (Figure A.3). This detector also has a responsivity that varies with wavelength, unlike the thermopile which has a flat response across the entire operating range. For laboratory grade PVs whose performance is not record-breaking, this technique is suitable.\(^{158}\) In the event of producing high performing devices, procedures for lamp calibration can be found elsewhere.\(^{159}\) The responsivity of the photodetector is multiplied by the corrected spectrum [whose integration value is 0.1W/cm\(^2\) - Figure A.9, Inset (A)], resulting in units that are given in Figure A.9, Inset (B). Integration of this spectrum

![Figure A.4: Inset (A) shows the average current measured as a function of wavelength. Inset (B) shows the average of the spectral irradiance after correcting for the responsivity of the photodiode.](image-url)
gives a total current density of $4.85 \times 10^{-5}$ A/cm$^2$. Multiplication of this response by the active area of the photodetector (1 cm$^2$) gives a predicted response of ca. 49 µA.

Figure A.5: Inset (A) shows the average current measured as a function of wavelength. Inset (B) shows the average of the spectral irradiance after correcting for the responsivity of the photodiode.

Figure A.6: Spectral irradiance of the light source after dispersion efficiency corrections.
Figure A.7: Inset (A) shows the transmission spectrum of the AM 1.5G filter used for standard Xe arc lamps. Inset (B) shows spectral irradiance after multiplication with the AM 1.5G optical filter.

Figure A.8: Inset (A) shows the integration of the spectrum prior to correction. Inset (B) shows the integration of the spectrum after the correction.
Figure A.9: Inset (A) shows the current density after multiplication of the corrected spectrum with the responsivity of the photodiode. Inset (B) shows the results after integration of the spectrum.
APPENDIX B: QUANTUM EFFICIENCY MEASUREMENTS

B.1 External Quantum Efficiency (EQE)

External quantum efficiency (EQE) measurements are used to determine the photoactivity of devices as a function of wavelength. The ideal photovoltaic device would have 100% EQE in the visible and near-IR region. However, recombination and charge-transfer losses prevent this ideality from taking place. We begin the process by assembling the proper instrumental components like that shown in Figure A.2. The Figure shows the diagram with all necessary focusing optics, which should match the F/# of the monochromator, along with the lock-in amplification system, iris’, and photodetector. Typically, lock-in amplification is not required. However, sources like xenon arcs contain a significant amount of signal spikes in the near-IR. These effects result in unreliable data being obtained if this is not compensated for. With respect to the photodetector, it should have good responsivity in the visible/near-IR region. It must be understood that what is being sought from this experiment is a spectrum which plots EQE as a function of wavelength. Take note that EQE is just the amount of electrons generated per incident photon. This requires information on the amount of photons that are striking the surface of the device and hence, Figure A.2 shows the instrumental setup with a commercial photodiode. A synopsis of the experiment is as follows: 1) Determination of spectral irradiance with the calibration photodiode, 2) Acquisition of EQE of the calibration photodiode, 3) Checking EQE of calibration photodiode against factory EQE, and 4) Determination of EQE of device.
The experiment is initiated by first obtaining the current being obtained from the photodiode as a function of wavelength incident from the monochromator. Good analytical practice calls for at least three measurements in total, resulting in the average current, which is just be the spectrum of the light collected [Figure A.4, Inset (A)]. The data obtained can now be used to solve for the spectral irradiance via the responsivity calibration of the detector. For example, if at 400 nm the average current was determined to be 2.14E-9 A, using the responsivity of the detector at 400 nm (1.42E-4 A/W), we obtain an average power of 1.51E-5 W, which leads to a Spectral Irradiance of 5.0E-5 W/cm²*nm when incorporating the area of 0.301 cm². Once this is done for all acquired wavelengths, the information on hand details the power arriving at the detector surface with respect to area and wavelength (assuming the distance from the monochromator is kept the same). This means that at this point, the calibration of the spectral irradiance is complete. Prior to switching to the device of interest however, good analytical practice calls for testing this calibration relative to the detector which was used. This is quite useful due to the cross checking that can be done with the factory calibration that was obtained with purchase of the photodiode. In other words, an EQE of the photodiode should be obtained and compared to the factory calibration.

Firstly, obtain another current vs. wavelength spectrum, which we will assume resulted in 7.1E-9 A/cm² at 400 nm. Secondly, let us assume that we are solving the EQE for the value obtained at 400 nm. We must first convert the spectral irradiance (mW/cm²*nm) into units of photons/s*cm²*nm, which is done by converting 400 nm into units of energy:
Where $h$ is Plank's constant, $c$ is the speed of light, $\lambda$ is the wavelength, and $J$ is energy in joules. The value obtained represents the amount of energy in one 400 nm photon. The spectral irradiance at 400 nm was determined to be $5.0E-5$ W/cm$^2$*nm, which can be converted into photons/s via:

$$\text{Watt} = \frac{\text{Joule}}{\text{second}}$$

$$\frac{5.0E-5 J * s^{-1} * cm^{-2} * nm^{-1}}{5.0E - 19 J}$$

$$1.0E14 \frac{\text{photons}}{cm^2 * nm * s}$$

With the value of photons already calculated, the number of electrons deriving from the interactions of the photons with the detector is determined. Knowing that the measured current density was $7.1E-9$ A/cm$^2$, we calculate via:

$$7.1E - 9 \frac{A}{cm^2 * nm} = 7.1E - 9 \frac{C}{cm^2 * nm * s}$$
Determination of the electrons now allows for the calculation of photons/electrons (EQE):

\[
7.1E - 9 \frac{C}{cm^2 * nm * s} \times \frac{1 \text{ electron}}{1.60E - 19 C} = 4.4E10 \frac{electrons}{cm^2 * nm * s}
\]

Determination of the electrons now allows for the calculation of photons/electrons (EQE):

\[
\left[ \frac{4.4E10 \text{ electrons} \cdot cm^{-2} \cdot nm^{-1} \cdot s^{-1}}{1.0E14 \text{ photon} \cdot cm^{-2} \cdot nm^{-1} \cdot s^{-1}} \right] \times 100\% = 0.044\%
\]

Another simpler route towards solving for EQE can be done by using:

\[
EQE = 1240 \frac{J_{sc}}{P_{in} \cdot \lambda}
\]

\[
= 1240 \frac{7.1E - 9}{5.0E - 5 \cdot 400} = 0.00044
\]

Where the 1240 derives from the unit conversion towards electrons and photons:

\[
EQE = h \cdot c \cdot \frac{J_{sc}}{P_{in} \cdot \lambda}
\]

\[
EQE = [(6.6E - 34 J \cdot s)(3.0E17 nm \cdot s^{-1})] \cdot \left[ \frac{A/ cm^2}{W/ cm^2 \cdot nm} \right]
\]
Using the factory calibration of the photodetector at 400 nm, which is the responsivity given in amps/watt, plugged into the EQE formula gives 0.0440169%. Calculating the residuals of the measured to the factory calculation over the entire spectrum should give an acceptable deviation nothing less than 1% for all points.

**B.2 Internal Quantum Efficiency (IQE)**

In the previous section, the external quantum efficiency was discussed, where it gives the amount of electrons per incident photons. Internal quantum efficiency (IQE) defines the amount of electrons generated per absorbed photons. Figure B.1 shows a normalized
IQE spectrum. For laboratory purposes, these plots are typically normalized due to values which deviate from the absolute. This is due to changes in the refractive index depending on the systems being used and not accounting for reflection losses. The experiment consist of obtaining the EQE of the device of interest, followed by the transmission spectrum of the active layers from the device. Subtracting the transmission from the maximum (100%) gives the total absorbed photons. Dividing the EQE by the percentage of absorbed photons results in the IQE.

B.3 Back-Calculating Photocurrent from EQE

Obtaining an EQE profile of a device leads to the ability for the use to predict the photocurrent that could be generated. However, it must be noted that EQE results are obtained under conditions that are not representative during J-V testing. For example, in EQE measurements, a nearly monochromatic flux of photons strikes the device under light intensities that are significantly lower than the intensities experienced during standard testing conditions (AM 1.5G). This results in the full set of conditions not being realized during the acquisition which results in back-calculated photocurrent values that are typically higher than those obtained during testing. The variation depends on many factors, but differences as high as 30% have been recorded over the term of this research tenure. Nonetheless, the exercise in back-calculating is helpful whenever back of the envelope calculations are needed to predict the behavior under AM 1.5G conditions if no source is available.
We begin the process by obtaining an EQE profile like the ones seen in Figure 4.16. This profile is typically covers the visible to near-IR range, which in this case was from 400 nm to 1100 nm. Next, obtain the spectral responsivity of the light source you would like to back-calculate from. The range of the spectral profile should cover the same range as the EQE spectrum. An example of the AM 1.5G can be seen in Figure A.1. As a sample calculation, we will use an EQE value of 34.8% from a generic device and a spectral irradiance of 8.4e-5 W/cm^2*nm from the light source obtained at 400 nm. First, begin by converting the wavelength unit (nm) into Electronvolts (eV).

\[
\frac{1240}{nm} = eV
\]

\[
\frac{1240}{400} = 3.1
\]

Where the derivation for the 1240 value can be found in Section B.1. Next, we convert the light source spectral irradiance value into units that can relate to spectral photon flux.

\[
Watts = \frac{Joules}{Second}
\]

\[
8.4 \times 10^{-5} \frac{W}{cm^2 * nm} = 8.4 \times 10^{-5} \frac{J}{cm^2 * s * nm}
\]

Next, we convert the irradiance into units of Electronvolts/cm^2*s*nm

\[
1 eV = 1.602 \times 10^{-19} J
\]

\[
8.4 \times 10^{-5} \frac{J}{cm^2 * s * nm} = 5.2 \times 10^{14} \frac{eV}{cm^2 * s * nm}
\]

Next, the amount of energy being put out (Solar Photon Flux) at the 400nm wavelength can be found by dividing the irradiance by the energy at which it was emitted (400 nm):
Next, conversion of the wavelength units into Electronvolts follows:

\[
\frac{1.7 \times 10^{14} \text{ Photons}}{\text{cm}^2 \cdot \text{s} \cdot \text{nm}} \cdot \frac{400 \text{ nm}}{3.1 \text{ eV}}
\]

\[
= 2.2 \times 10^{16} \frac{\text{Photons}}{\text{cm}^2 \cdot \text{s} \cdot \text{eV}}
\]

The completion of these calculations gives the amount of energy per unit area, time, and energy. We now multiply the EQE quantity by the incident quantity to give the amount of electrons per unit area, unit, time and energy:

\[
= 0.348 \frac{\text{Electrons}}{\text{Photons}} \cdot 2.2 \times 10^{16} \frac{\text{Photons}}{\text{cm}^2 \cdot \text{s} \cdot \text{eV}}
\]

\[
= 7.6 \times 10^{15} \frac{\text{Electrons}}{\text{cm}^2 \cdot \text{s} \cdot \text{eV}}
\]

The sample calculation displayed above is only for one unit wavelength. Assuming that an entire area has been sampled, a plot of the quantity versus the energy is created [Figure B1-Inset (A)]. This spectrum is then integrated to give the area under the curve to give the charge over the range of energy [Figure B1-Inset (B)], which can then be multiplied by the elementary charge (Coulomb = 1.602 x 10^{-19}) to give the current density in amps/unit area.
Figure B.1: Inset (A) the plot of device response versus energy. Inset (B) shows the integration of the spectrum in Inset (A).
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