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Eco-friendly and Scalable Fabrication of Organic Optoelectronic Sensors

By

Jasmine Mimi Jan

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Engineering - Electrical Engineering and Computer Sciences

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Ana Claudia Arias, Chair

Professor Grigory Tikhomirov

Professor Naomi Ginsberg

Summer 2024

Eco-friendly and Scalable Fabrication of Organic Optoelectronic Sensors

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Jasmine Mimi Jan

Abstract

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Doctor of Philosophy in Engineering - Electrical Engineering and Computer Sciences

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Organic electronics have gained popularity due to their potential to revolutionize electronic technologies with improved performance, low cost, and unique applications in flexible and wearable systems. A significant advantage of organic electronics is their solution solubility, which enables cost-effective and additive printing processes, reducing material waste and facilitating large-area manufacturing. This thesis will present work towards developing eco-friendly and scalable organic optoelectronic sensors. Organic light-emitting diodes (OLEDs) and organic photodiodes (OPDs) are demonstrated as photoplethysmography (PPG) sensors, representing steps toward lightweight and flexible pulse oximeters. A scalable blade coating method is used to simultaneously print OLEDs and OPDs on a single substrate, simplifying fabrication while maintaining device performance of both devices. Finally, solution and film optimizations are used to replace toxic solvents with a greener solvent in organic photovoltaics (OPVs), demonstrating critical steps towards eco-friendly fabrication of organic electronics.

To my family and friends.

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After the pandemic, our group consolidated to SWARM on the fourth floor of Cory Hall. During this time, I began meeting many more people from different labs, including Rebekah Zhao, Ekin Karasan, Alfredo De Goyeneche, Ryan Kaveh, Shreya Ramachandran, Suma Anand, Yu-Chi Lin, Jade Pinkenburg, Liz Murray, Lydia Lee, Micah Roschelle, Rozhan Rabbani, and many others. I also interacted much more closely with the other half of our group including: Carol Baumbauer, Payton Goodrich, Anju Toor. Because we had to walk through the entire office to reach our lab, I would often stop to chat with someone along the way. Whether it was in the lab, in the kitchen, or in over the cubicle walls, I was always met with a friendly face and lots of laughter. The last several years of my PhD were spent in SWARM during which new members joined our group: Yuhan Wen, Julian Maravilla, Maykel Nijenhuis, Sophie Koh, Lucas Lahann, Carolyn Schwendeman, Philothei Sahinidis, Carla Milsted, and Yuting Cai. As a group, we bonded over shared experiences, food, and general shenanigans. I look back on the memories I have in this space with great fondness. I’m so glad to have grown close to many individuals, who I’m sure I will remain close with for many years after my PhD.

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Chapter 1

Introduction

Organic electronics have grown in popularity due to its potential to revolutionize electronic technologies in terms of performance, low cost, and unique applications in flexible and wearable systems [1–7]. In particular, organic optoelectronics are increasingly prominent due to their wide range of applications in lighting and sensing applications spanning from consumer displays to lightweight photosensors [8–10]. Compared to inorganic semiconductor materials that require expensive vacuum and lithography fabrication, the solution solubility of organic semiconductors enables fabrication with simple and cost-effective fabrication through solution processing. A major advantage of solution-processable electronics is the use of additive printing processes to reduce material waste and facilitate large-area manufacturing techniques [11–14]. Furthermore, the low-temperature deposition of organic semiconductors are compatible with a variety of flexible substrates, making them ideal for applications where flexibility and conformity are necessary [15–18]. In recent years, increased efforts have been made to enhance the commercial viability of organic electronics and sensors by supporting scalable printing techniques and minimizing reliance on toxic solvents [19–22]. These advancements are pivotal in addressing the economic and environmental challenges associated with electronics manufacturing. With increased economical interest and steps towards reduced environmental impact of organic electronics, its promising capabilities pave the way for significant advancements in consumer products, renewable energy solutions, and next-generation technologies.

1.1 Optoelectronic Devices and Figures of Merit

1.1.1 Organic Semiconductors

Organic semiconductors are carbon-rich materials that possess semiconducting properties. In contrast to inorganic compounds, organic compounds comprise of at least one carbon-hydrogen bond. The semiconducting nature of organic molecules arise from

the conjugated molecular structures where alternating single and double bonds lead to the formation of hybridized sp^2 orbitals. A carbon-carbon double bond comprises of two bonds: a sigma bond from the overlap of the sp^2 hybridized orbitals and a π bond from the overlap of the unhybridized p orbitals. The π bonds give organic semiconductors their unique optical and electrical properties. The charge carrier mobilities of organic semiconductors will depend on the ability of π -electrons to move through the conjugated system influenced by molecular packing and crystallinity [23–25]. Organic semiconductors typically exhibit lower mobilities than inorganic semiconductors due to incoherent hopping of charges from one molecule to the next [24, 26–28]. Their low dielectric constant also results in bound electron-hole pairs known as excitons when photons are absorbed. Conversely, upon injection of electrons and holes, excitons are first formed before recombining [29–31]. Finally, the molecular orbitals are filled in increasing energy levels, forming the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The energy gap between HOMO and LUMO defines the semiconducting properties of the material, analogous to the valence and conduction bands in traditional semiconductors. An illustration of molecular orbitals and the energy levels contributing to semiconducting properties are shown in Figure 1.1.

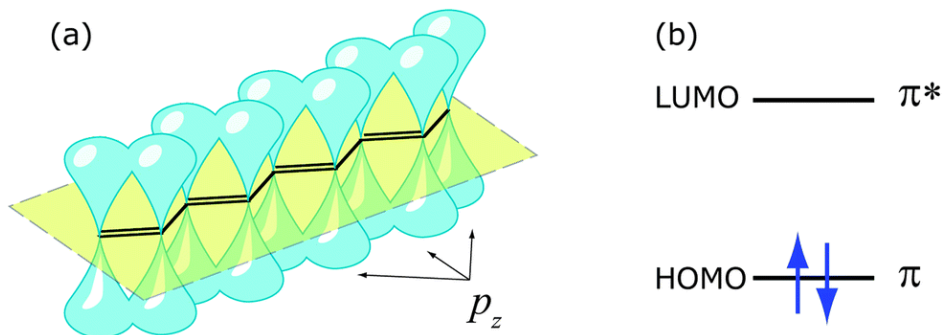


Figure 1.1: Illustration of molecular orbitals of an organic compound. (a) A conjugated backbone with overlapping p_z orbitals that point out of the molecular plane. (b) Highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). Arrows denote two electrons with different spins. Figure from Miknenko (2015) [30].

The energy band gap is a fundamental property that influences the optical and electrical properties of optoelectronic devices [29, 30, 32]. In terms of optical properties, the band gap determines the color of the light emitted by light emitting diodes. For light absorbing devices, the band gap determines the spectra of incident light absorbed, resulting in photogenerated excitons. In terms of electrical properties, the positions of the HOMO and LUMO levels also influence the ease with which electrons and holes can transport within the device. The relative positions of HOMO and LUMO levels between adjacent materials can impact

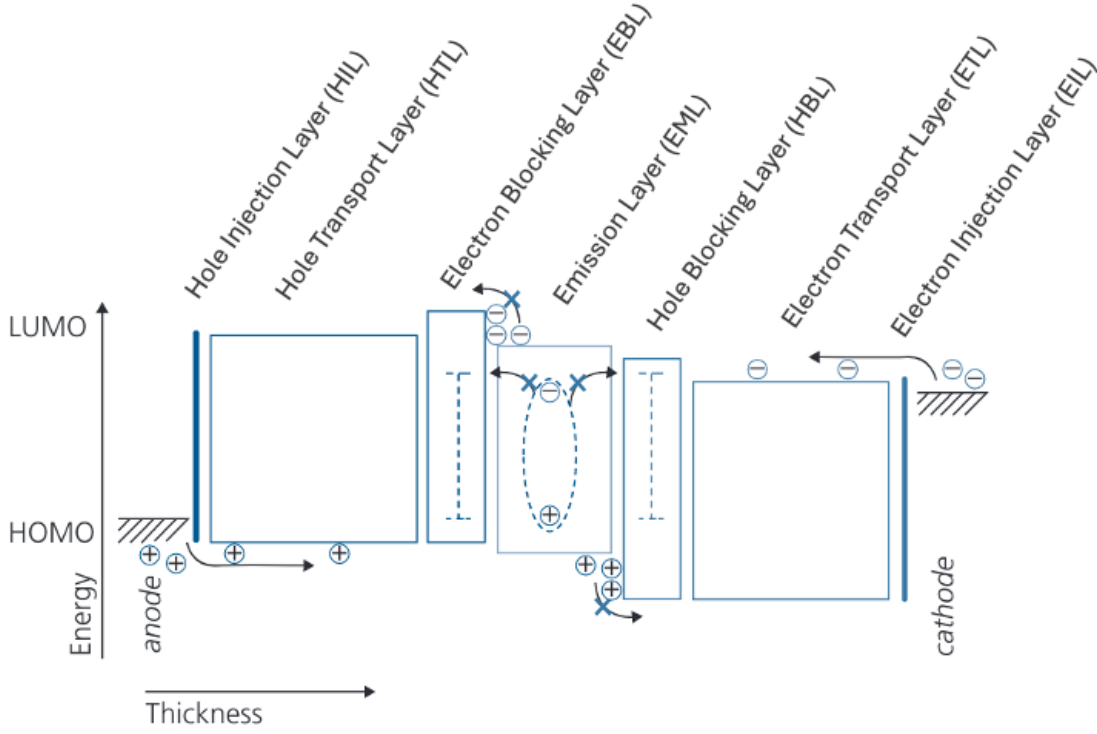


Figure 1.2: Diagram of a multilayer OLED employing interlayers: HIL (hole injection layer), HTL (hole transport layer), EBL (electron blocking layer), EML (emission layer), hole blocking layer (HBL), electron transport layer (ETL), and electron injection layer (EIL). The HIL and EIL help assist in injection of charges from the anode and cathode energy levels into the HTL and ETL, respectively. The EBL and HBL assist in confining the holes and electrons within the EML. Figure from [32].

charge injection, transport, and recombination [24, 33, 34]. Charge injection layers and charge transport layers are additional materials, often categorized as interlayers, that help facilitate efficient charge transport and minimize energy barriers between the active layer and anode/cathode contacts. For instance, OLEDs rely on efficient charge injection from associated anodes and cathodes towards the light emission layer. Interlayers are commonly added adjacent to the emission layer to arrange energy level cascading, enabling smooth transport of charges. This is shown in a energy band diagram of a multilayer OLED in Figure 1.2. Furthermore, blocking layers with shallow LUMO or deep HOMO levels can be used to confine electrons and holes to the EML for recombination and prevent losses in emission.

The combination of optical and electrical properties determined by the band gap

ultimately influences the efficiency of the device [24, 33, 34]. In optoelectronic devices, this refers to the conversion of optical to electrical energy (or vice versa). Furthermore, because the energy band gap is determined by the molecular structure of the semiconductor material, chemical synthesis strategies and molecular engineering can modify the optical and electrical properties of a semiconductor for specific characteristics and applications [23, 35, 36]. For instance, organic light-emitting diodes (OLEDs) can be engineered to emit light of specific colors and intensities, enabling high color purity for display technologies [37]. Similarly, organic photo-absorbing materials have been designed to broaden their absorption spectrum to increase response to the incident light for use in high efficiency solar cells and high responsivity photodiodes [38, 39].

1.1.2 Organic Light-Emitting Diodes

The most prominent success in organic semiconductor technologies is the emergence of high-end OLED displays [32]. At the time of writing, these displays are the predominant display technology used in consumer electronic devices including smart phones, tablets, laptops, televisions, wearable technologies, digital cameras and augmented/virtual reality headsets [40]. Commercial interest in OLED displays have grown as they possess brilliant emission colors, very high on/off contrast ratio, and the ability to be shaped for a particular aesthetic or practical purposes [41].

OLEDs are electroluminescent sources in that current injection from the cathode and anode contacts generates an exciton on the emissive molecules within the structure, leading to radiative recombination and light emission. OLED light emission is primarily understood as a four step process as shown in Figure 1.3. Typically the emission layer (EML) will be sandwiched by interlayers for transporting or injecting a corresponding charge [30]. The purpose of these interlayers are to enhance charge injection from the electrode contacts and assist in localizing the recombination in the EML [41, 42]. During operation, the hole and electron charges are first injected from opposing contacts. Second, the charges are transported via electric field towards the EML. Here, thin hole blocking or electron blocking layers may also be present to further localize the charges in the EML. Third, a hole on the HOMO and an electron on the LUMO form a bound exciton. Finally, radiative recombination of the exciton emits light that emerges via the transparent anode and substrate for bottom emitting devices. A typical film stack for a single OLED device with various interlayers and direction of light emission is shown in Figure 1.4.

OLEDs are light emitters that are commonly used in visual applications such as lighting and displays. As such, the optical performance of OLEDs requires consideration of how the human eye behaves and receives various forms of light. This is known as photometry [41]. The figures of merit used to assess OLED performance can be both radiometric and photometric. Benchmarks for measuring light emission are irradiance, radiance, and luminance. **Irradiance** E , with units of $W \cdot m^{-2}$, is defined as the radiant flux per unit

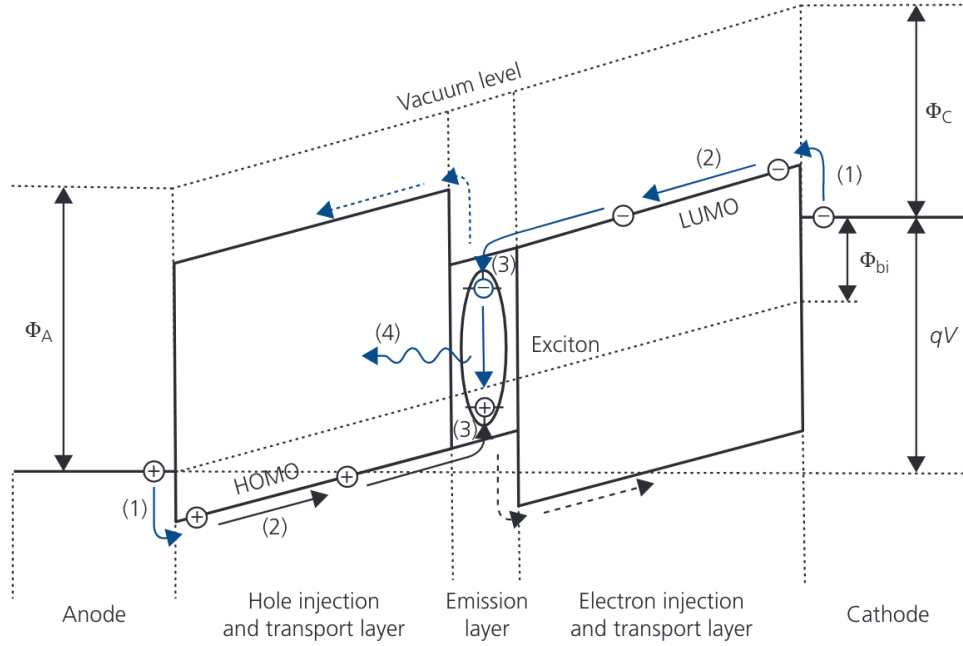


Figure 1.3: Illustration of the four steps of electroluminescence generation in a biased OLED structure. 1) The hole and electron are injected from opposing contacts. 2) The charges are transported towards the emission layer via the applied electric field. 3) The hole and electron form a bound exciton. 4) The exciton radiatively recombines to emit light. Figure adapted from Brutting (2013) [42].

area emerging from a point in a given surface. It is defined below where ds_0 is the surface area element on the surface of interest. **Radiance** L is the amount of radiant flux per unit area, per unit solid angle emerging from a point on the surface of interest in units of $Wm^{-2}sr^{-1}$. It is defined in 1.2 where ω is defined as the solid angle in a specific direction and s is the projected area onto the surface containing the point of interest. **Luminance**, L_v , in units of candela per meter squared, $cd \cdot m^{-2}$, is a photometric measure of radiance $L(\lambda)$ and is a critical parameter for lighting and display applications. Because the human eye has a particular spectral response to radiation, a standardized spectral response has been set by the Commission Internationale de l'Eclairage (CIE). This is known as the **photopic response**, $V(\lambda)$, and is shown in Figure 1.5. The photopic response is used to convert radiometric quantities to eye response-weighted photometric equivalent quantities given the increased varying sensitivities of wavelengths to the human-eye. Thus, photometric quantities are typically denoted with a “v” to indicate a human-eye weighted response. Equation 1.3 shows how to derive the metric where $V(\lambda)$ is the photopic response, I_{det} is the measured photocurrent at the detector, D is the distance between the OLED and the detector, $R_{det,s}$

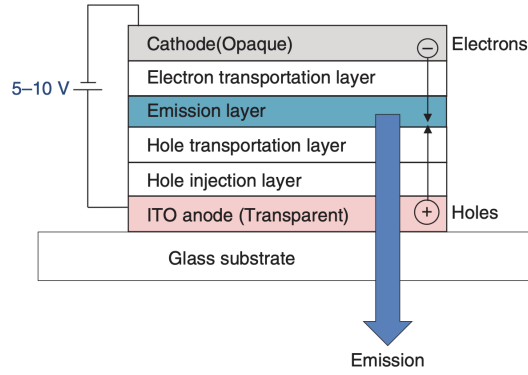


Figure 1.4: Example of an OLED device with electrode transport layer (ETL), emission layer (EML), hole transport layer (HTL), and hole injection layer (HIL). Figure from Forrest (2020) [32].

is the detector responsivity weighted to the measured OLED emission spectrum, S_0 is the OLED emission area, and A_0 is the detector area.

$$E = \frac{d\Phi}{ds_0} \quad (1.1)$$

$$L = \frac{d^2\Phi}{d\omega ds} \quad (1.2)$$

$$L_v = 683 \left[\frac{\text{lm}}{\text{W}} \right] \int_{380}^{770} L(\lambda) V(\lambda) d\lambda \quad (1.3)$$

$$L(\lambda) = \frac{I_{det} D^2}{R_{det,s}(\lambda) S_0 A_0} \quad (1.4)$$

The benchmarks regarding the electrical operation required of OLEDs are often characterized by the turn-on voltage and the operating current. **Turn-on voltage**, the minimum voltage required for the OLED to start emitting light is typically defined as bias voltage required for an emission of $10 \text{ cd} \cdot \text{m}^{-2}$ from the OLED. The operating current or voltage can be selected based on the target application, however, a common specification

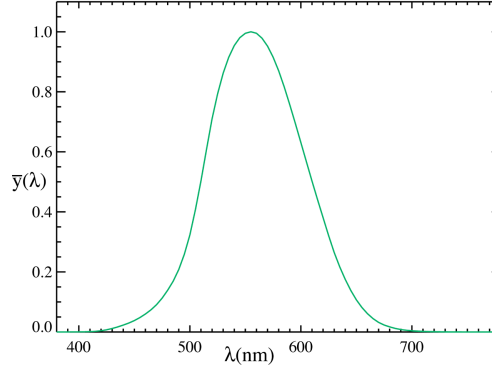


Figure 1.5: Commonly referred to as the photopic response, the 1931 CIE luminosity function describes the photopic vision of humans.

is the operating current or voltage required for a luminance of $1000 \text{ cd} \cdot \text{m}^{-2}$. This allows standard comparisons between different OLED devices.

Electroluminescence and CIE color coordinates characterize the color output of the OLED in response to electrical input. This is critical for meeting application requirements. For instance, the color space of RGB displays will consider the precise emission wavelengths and color purity of OLEDs to ensure accurate and vibrant color reproduction. Electroluminescence is typically plotted with intensity versus wavelength at a fixed applied bias or current. Using the electroluminescence spectrum, the color output of the OLED can be assessed. The 1931 CIE Color System is a trichromatic system based on the primary colors of red, green, and blue. The weighting functions roughly corresponding to those three primary colors are denoted $\bar{x}$, $\bar{y}$, and $\bar{z}$ and are shown in 1.6. Using these weighting functions, a set of tristimulus values X, Y, and Z are obtained with the following:

$$X = \int_{380}^{780} S(\lambda) \bar{x}(\lambda) d\lambda \quad (1.5)$$

$$Y = \int_{380}^{780} S(\lambda) \bar{y}(\lambda) d\lambda \quad (1.6)$$

$$Z = \int_{380}^{780} S(\lambda) \bar{z}(\lambda) d\lambda \quad (1.7)$$

Efficiency is an important metric to deduce illumination quality, energy efficiency, and longevity of an optoelectronic device. It influences energy consumption, cost savings, environmental impact, and the ability to use the device in various applications where energy

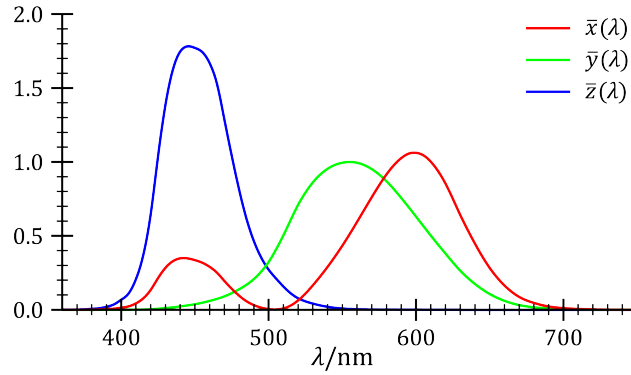


Figure 1.6: 1931 CIE Color Matching Functions with $\bar{x}$, $\bar{y}$, and $\bar{z}$ corresponding to the primary colors: red, green, and blue.

use can be restricted. There are various ways to consider the efficiency of light emitters. **External Quantum Efficiency**, EQE , is a commonly used metric for optoelectronic devices. In the context of emitters, EQE , refers to the ratio of photons emitted from the device, n_{ph} , and the electrons injected to produce the photons, n_e , shown in equation 1.8. **Current Efficacy**, η_I , is useful in circuit design for display applications where OLED pixels are driven by current. It is defined in 1.9 where J is the current density in $mA \cdot cm^{-2}$. **Luminous Efficacy**, K_r , is expressed in lumens per Watt, and characterizes the effectiveness of a beam of radiation for stimulating a response in the human eye. It is defined as the ratio of luminous flux ϕ_v , in lumens, and radiant flux ϕ in Watts. Finally, **Power Efficacy**, K_s , is the measure of luminous flux produced by the device at a particular electrical power input. It is defined in equation 1.12 where ϕ_v is the luminous flux in $lm \cdot W^{-1}$ and P is the electrical power input in Watts.

$$\eta_{EQE} = \frac{n_{ph}}{n_e} 100\% \quad (1.8)$$

$$\eta_I = 0.1 \frac{L_v}{J} \quad (1.9)$$

$$K_r = \frac{\Phi_v}{\Phi} \quad (1.10)$$

$$\Phi_v = 683 \left[\frac{lm}{W} \right] \int_{380}^{770} \Phi(\lambda) V(\lambda) d\lambda \quad (1.11)$$

$$K_s = \frac{\phi_v}{P} \quad (1.12)$$

1.1.3 Organic Photodiodes

While OLEDs have rose in prominence in commercial displays, other organic devices have also gained popularity in organic electronic research. Organic photodiodes (OPDs) are of particular interest for their broad spectral response ranging from ultraviolet to near infrared (NIR) wavelengths (300 nm to 1500 nm)[43]. Their ease of scalable fabrication are also advantageous for large area image sensors[43–46]. The photoabsorbing layer of an organic photodiode uses donor and acceptor materials with LUMO and HOMO that serve as electron and hole transporting bands. The donor is hole accepting, while the acceptor is electron accepting. Similar to OLED architectures, photodiodes will employ a a sandwich architecture with an anode and cathode surrounding the photoactive layer with additional interlayers to assist charge injection and transport.

Typically photodiodes are operated under reverse bias to increase charge collection efficiency and increase the detector bandwidth by accelerating photogenerated charges with the applied electric field. When operated in reverse bias, the photodiode is in photodetector mode. Alternatively, the photodiode may also operate under no bias, relying on the internal field to separate and collect charges. Under this operation, the photodiode is in photovoltaic mode. The photodiode relies on the heterojunction to separate a photogenerated exciton. Most organic photodiodes employ a bulk heterojunction (BHJ) active layer, a mixture of donor and acceptor materials in a single film. The mixture of donor and acceptor materials increases the surface area across which excitons can be dissociated. An example of the bulk heterojunction can be see in Figure 1.7 where the bulk heterojunction consists of an interpenetrating network of donor and acceptor domains ideal for dissociating photogenerated excitons.

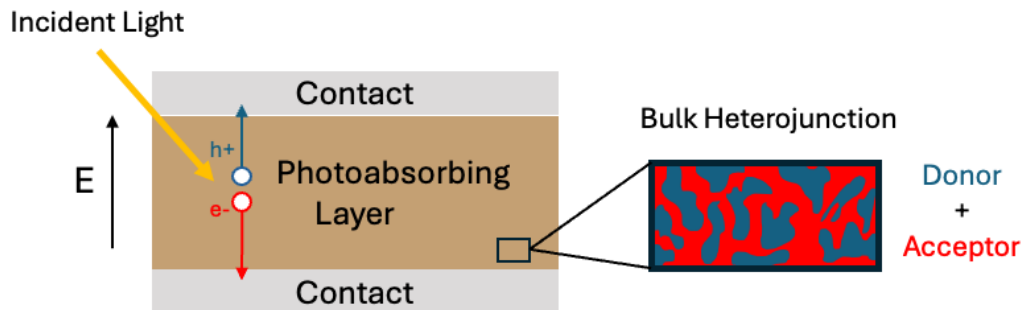


Figure 1.7: Illustration of a donor and acceptor blend mixed to form an active layer in a photoabsorbing device. The interpenetrating donor and acceptor materials within the bulk heterojunction allows holes and electrons to dissociate and drift towards their respective contacts.

Photogeneration and charge collection relies on the energy bands within the photoabsorbing material. First, absorption of a photon with energy greater than the energy band in either the donor or acceptor generates an exciton. Second, this exciton will diffuse towards the donor-acceptor junction. Third, at the heterojunction, bound electron and hole are transferred to the respective domain (electron from donor to acceptor and hole from acceptor to donor depending on where the exciton originated). This transfer is driven by the offset energies of the LUMOs and HOMOs of the two layers. Finally, the electron and hole dissociates to drift towards their respective electrode contact. The full mechanism of can be seen in Figure 1.8. In contrast to many inorganic materials where absorption results in free carriers, organic semiconductors proceed through photogeneration via generation and dissociation of coulombically bound excitons. Thus, organic photodetectors inherently possess more inefficient photogeneration steps and require a heterojunction to provide the necessary energy potential for exciton dissociation.

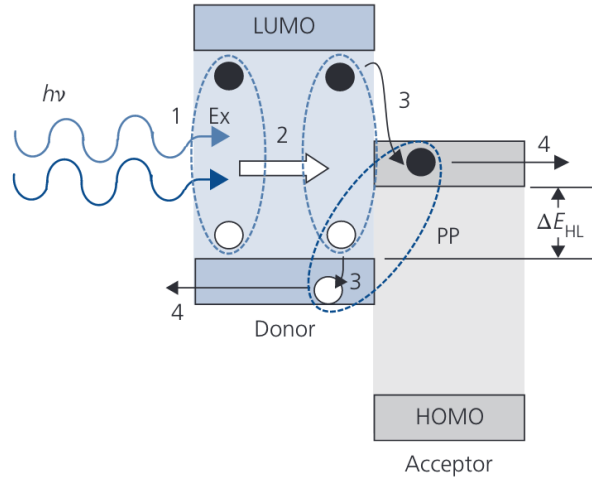


Figure 1.8: Four step process of photogeneration in a photodetector. 1) Photogeneration of an exciton 2) Diffusion of exciton towards the donor-acceptor junction 3) Transfer of charge (electron goes to acceptor and hole goes to donor) 4) The bound hole and electron pair dissociate to travel freely towards their respective electrode contacts. Figure from Forrest (2020) [32].

High performance OPDs have been fabricated with industrially relevant coating and printing techniques, motivating their use in applications where low-cost high-throughput sensors are needed. For instance, printed OPDs have been incorporated to various systems such as lab-on-chip systems, optical communication, medical sensors, spectrometers, and image sensors [43, 47–49]. As photodiodes are used in optical detection, it is important that

the photodiode has excellent speed response, linearity, as well as spectral response. Figure 1.9 shows highlights common benchmarks for organic photodiodes.

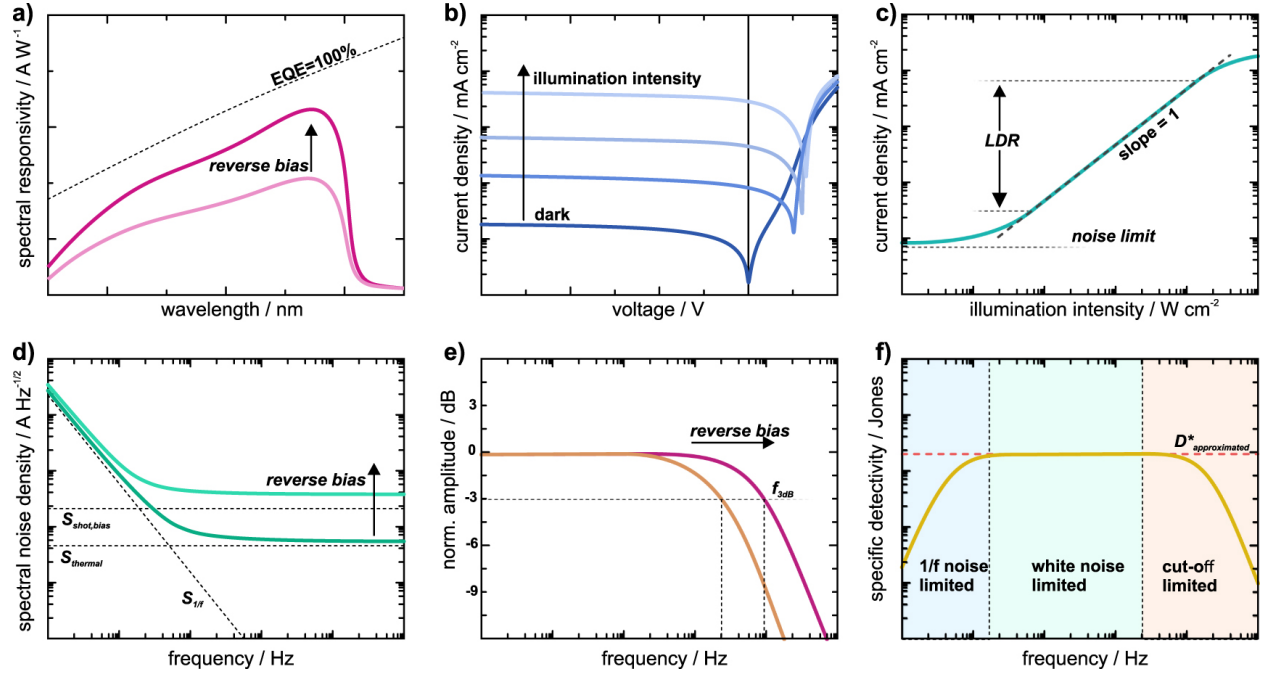


Figure 1.9: Schematic of the OPD figures of merit and characteristics as a function of reverse bias or illumination intensity. (a) Spectral responsivity $R(\lambda)$, (b) JV curve for different illumination intensities, (c) the linear dynamic range (LDR), (d) noise spectral density S_{noise} (f) and its theoretical limits (shot, thermal, and $1/f$ noise), (e) $R(\lambda)$ attenuation in dB as a function of excitation frequency. The -3 dB-cutoff frequency is marked as dotted line. (f) The frequency dependent specific detectivity D^* and the approximated frequency independent D^* approximated in different regimes of operation. Figure from Strobel (2019)[14].

The optimal photodiode will have a high contrast between its photogenerated current and its dark current. **Dark Current**, J_d , refers to the flow of current in the absence of any external illumination. This current is primarily caused by thermally generated carriers within the semiconductor material of the photodiode and directly affects the signal-to-noise ratio and sensitivity of the photodiode. Increased dark current can arise from increase in temperature as the dark current increases exponentially with temperature due to the increased thermal energy available to generate electron-hole pairs. A method to minimize dark current is to reduce thermally generated carriers by selecting larger bandgap materials or by optimizing film thickness to increase recombination of generated carrier prior to charge

collection. Dark current is typically reported under negative or zero bias. In the same vein, specific detectivity is a benchmark for performance of a photodiode at low irradiances is specific detectivity. **Specific Detectivity**, $D^*(\lambda)$, is the reciprocal optical power required for a signal-to-noise ratio of unity, normalized to the device area. This represents the ability of the OPD to detect an optical signal and generate a signal current, measured in Jones, or $[cmHz^{1/2}W^{-1}]$. The expression for $D^*(\lambda)$ where R is responsivity, S is noise spectral density, A is the device area, J_d is the dark current, λ is wavelength, and h , c , and q_e are physical constants plank's constant, speed of light, and elementary charge, respectively. It is commonly assumed that shot noise is the main contributor to noise, however, it is commonly known that this can lead to an overestimation of detectivity. Thus, this assumption should be stated explicitly.

$$D^*(\lambda) = \frac{R(\lambda)}{S} \sqrt{A} = \frac{R(\lambda)}{\sqrt{2q_e J_d}} \quad (1.13)$$

The spectral response of the photodiode is a key parameter determining its use in various applications as photogeneration may be required at specific wavelengths of incident light. **External Quantum Efficiency**, EQE , describes ratio between the number of total electrons collected and number of incident photons. This is typically plotted as a function wavelength as EQE can vary across wavelengths. For OPDs, the EQE is the inverse of the same equation for OLEDs. Alternatively, it may be useful to view the incident light as an input of power rather than photons. **Spectral responsivity**, $R(\lambda)$ of a photodiode determines the application space of a photodetector as it quantifies the electrical output of a detector in response to optical power over a range of wavelengths. $R(\lambda)$, in units of $A \cdot W^{-1}$, is defined as the ratio between photocurrent generated I_L and incident optical power P_L as a function of wavelength. In equation 1.15, η_{EQE} is the external quantum efficiency of the detector for a given wavelength, q is the elementary charge, f is the frequency of the incident light, h is Planck's constant, and c is the speed of light. This metric can be calculated from the measured EQE .

$$\eta_{EQE} = \frac{n_e}{n_{ph}} 100\% \quad (1.14)$$

$$R(\lambda) = \frac{I_L}{P_L} = \frac{\eta_{EQE} q}{hf} = \frac{\eta q \lambda}{hc} \quad (1.15)$$

Finally, benchmarks describing more application specific requirements are linear dynamic range and frequency response. **Linear Dynamic Range**, *LDR*, describes the range of intensities in which the detector’s electrical response is linear to incident illumination. A wide linear dynamic range ensures accurate and precise measurements across a broad range of input light irradiances. It can be used as a calibration to correlate measured photocurrent with incident light power. It is typically measured and reported at one wavelength of light. **Frequency Response**, or cut-off frequency, f_{-3dB} , is defined as the frequency at which output power of the detector is attenuated by 50% in response to modulating light signals. Similar to linear dynamic range, this metric is also typically measured and reported at one wavelength of light. A wider frequency response may be desired as it represents the device’s ability to reproduce or transmit input light signals at higher frequencies.

$$LDR = 20 \cdot \log \left(\frac{i_{\text{lin,max}}}{i_{\text{lin,min}}} \right) \quad (1.16)$$

$$-3 \text{ dB} = 20 \cdot \log \left(\frac{i(f_{-3\text{dB}})}{i_0} \right) \quad (1.17)$$

1.1.4 Organic Solar Cells

While OPDs have distinct advantages for optical detection, a great deal of effort in research has focused on developing organic solar cells, also known as organic photovoltaics (OPVs). Solar cells need to maximize power output by generating charges from all available photons, typically along the solar spectrum. As the solar spectrum primarily possesses visible and NIR spectra, it is important that both donor and acceptor layers can absorb in those broad wavelengths [50]. However, it is common that donor and acceptor materials are combined in such a way to be complementary in their absorption [38, 51, 52]. However, selective absorption in a particular region of UV or non-visible wavelengths also enable the potential for semitransparent OPVs to be used in window and building applications [38]. Organic solar cells are classified in the third generation of solar technology along with dye sensitized, quantum dot sensitized and perovskite solar cells [53]. Flexibility and low cost deposition on large substrates has motivated interest in organic solar cells [54–57]. In addition, the materials used in other panels and modules contain toxic and costly previous metals, creating concerns over recyclability and end of life disposal [58]. The National Renewable Energy Laboratory (NREL) efficiency chart shows that OPV technology has matured quickly with efficiencies nearly reaching 20% in recent years [59–63].

OPVs are functionally similar to organic photodiodes in that they produce current upon exposure to light and often use the same materials and device architectures. However, the distinguishing factor of OPVs from OPDs is the application in which they are used. While OPDs are often used for detection of low light settings, OPVs are commonly used to convert broad spectrum light (outdoors or lighting indoors) to electrical energy [64, 65]. The most critical metric for solar cells, or photovoltaics, is the power conversion efficiency (PCE), describing the efficiency with which the device converts incident light into electrical energy. This critical metric, along with others, are easily derived from a current-voltage sweep. The IV curve of a solar cell is the superposition of the IV curve of a diode in the dark with the light-generated current. Below is the ideal diode equation adjusted to account for the generation of current from illumination, I_L .

$$I = I_0 \left[\exp \frac{qV}{nKT} - 1 \right] - I_L \quad (1.18)$$

Several important benchmarks are used to compare solar cell performances. The first figures of merit relate to the current-voltage characteristics of a solar cell, shown in Figure 1.10. **Short circuit current**, I_{sc} , is the current through the solar cell when the voltage across the solar cell is zero. This current describes the photovoltaic effect: the generation and collection of light-generated carriers under illumination. The short-circuit current is the largest current which may be drawn from the solar cell. I_{sc} depends on the area of the solar cell, the intensity of light, the spectrum of light, the spectral response of the cell, and optical properties of the cell. Often times, this value will be reported as the short circuit current density, J_{sc} , where the short circuit current will be normalized to the device area. The short circuit current can also be calculated by integrating the solar cell's *EQE* over the incident light's spectrum, typically referred to as the spectrum integrated short circuit current. Often this calculated current is reported to ensure integrity of IV curve measurements [66–68]. **Open circuit voltage**, V_{oc} , is the voltage at which the dark current and photocurrent are equal and opposite, resulting in no net current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell required to counteract the light-generated current. When a load is connected to the cell, the operating point will occur along the IV curve between the open-circuit and short-circuit conditions. This point will be determined by the load resistance. Ideally, this occurs at the **maximum power point**, P_{MP} , shown in Figure 1.10. P_{MP} represents the point at which output power is maximized along the IV curve.

Using the previous values of I_{sc} , V_{oc} , P_{MP} further solar cell analysis can be done to understand where power losses may arise. **Fill factor** effectively quantifies the “squareness” of the IV curve. It quantifies the relative power that can be generated from a solar cell compared to its theoretical maximum power output, the product of I_{sc} and V_{oc} . Fill factor is calculated in equation 1.19 with P_{MP} , I_{MP} and V_{MP} . The **power conversion efficiency**,

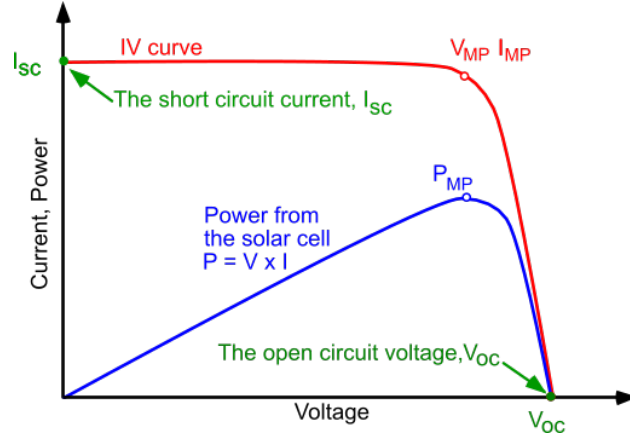


Figure 1.10: The current-voltage (IV) characteristics (red) and power-voltage curve (blue) of a solar cell under illumination. The short circuit current and open circuit voltage is shown at points along the IV curve. The maximum power point is shown on the power-voltage curve. Figure from PVEducation [69].

PCE, is the most critical metric reported in solar cell research. The power conversion efficiency is defined as the ratio of energy output from the solar cell to input energy. It is calculated using the equation 1.20. Because this metric depends on the light intensity of the input source, the environment in which the cell is measured must be reported as well. In a laboratory setting, this is typically AM1.5G conditions at 1 sun ($100mW \cdot cm^{-2}$) illumination at room temperature. AM1.5GG, or Air Mass 1.5 Global, is a standard spectrum used to simulate solar radiation on the Earth's surface for testing and comparing the performance of solar cells and photovoltaic devices. It represents the solar spectrum after it has passed through the Earth's atmosphere. The spectral irradiance of AM1.5G and an example of a solar simulator used for laboratory measurements is shown in Figure 1.11.

$$FF = \frac{P_{MP}}{V_{oc} \cdot I_{sc}} = \frac{I_{MP} \cdot V_{MP}}{V_{oc} \cdot I_{sc}} \quad (1.19)$$

$$PCE = \frac{P_{out}}{P_{in}} = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}} \quad (1.20)$$

To account for the non-idealities in a solar cell, two parasitic resistances considered [64, 70]. A model of a non-ideal solar cell can be seen in 1.12, showing a shunt resistance and a series resistance. These two parasitic resistances represent the primary methods of losses in

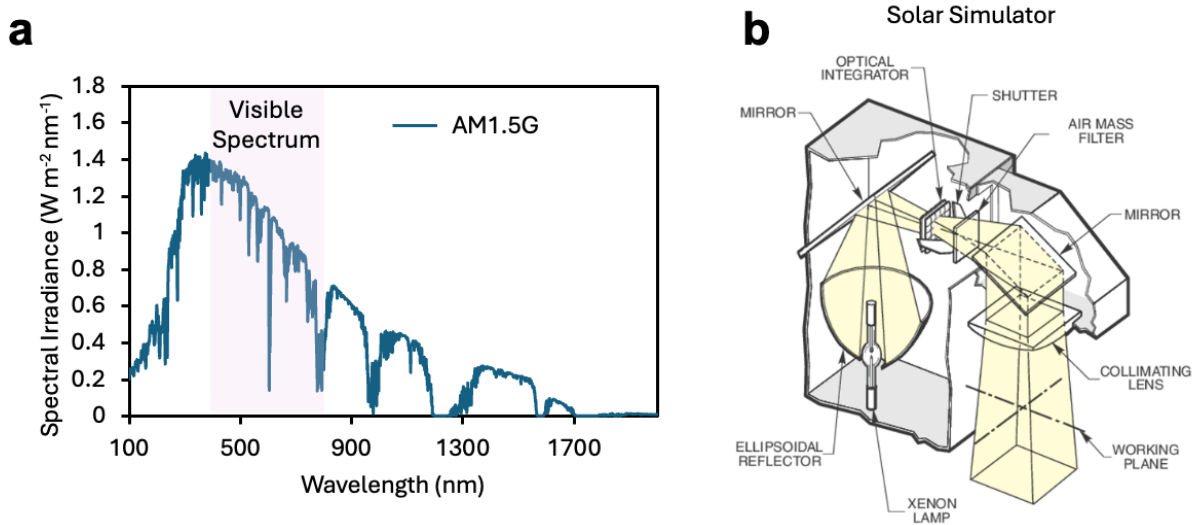


Figure 1.11: a) The spectral irradiance of sunlight conditions, both direct and scattered, at a solar zenith angle of 48.2 degrees above the horizon (AM1.5G). The visible spectrum is highlighted for reference. b) Illustration of solar simulator used in laboratory settings to measure fabricated solar cells. The emission of a xenon lamp is passed through an air mass filter to mimic the conditions of sunlight passing through the earth's atmosphere.

the efficiency of a solar cell arising from components of the solar cell structure, such as the semiconductor material, metal contacts, and interconnects [71]. Series resistance does not affect the solar cell at open-circuit voltage, however, near the open-circuit voltage, the IV curve is strongly affected by the series resistance. Series resistance is typically calculated from the slope of the IV curve at the open-circuit voltage point. This resistance can arise from bulk, contact, and sheet resistances in the device. Shunt resistance, on the other hand, are typically due to manufacturing defects resulting in low resistance paths where light-generated current to bypass the intended current path. Crystal defects, edge effects, and junction leakage can lead to low shunt resistances. The effect of shunt resistance is more severe in dim conditions where there is less light generated current [72]. At low voltages where the effective resistance of the solar cell is high, the impact of a resistance in parallel is large. The shunt resistance is typically calculated from the slope of the IV curve at the short-circuit point. Thus, analysis of parasitic resistances can serve informing and analyzing losses in solar cells.

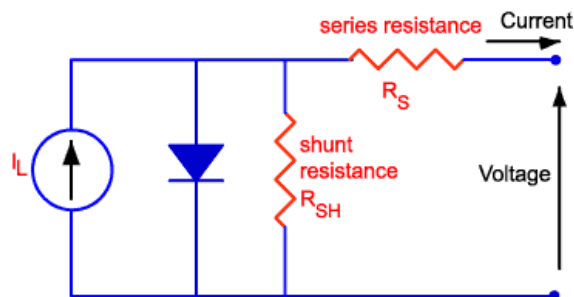


Figure 1.12: Standard equivalent circuit model of a solar cell. The current source represents the photogenerated current of the solar cell. Two parasitic resistances are added to the model: series resistance and shunt resistance. Figure from PVEducation [69].

1.2 Sensor Applications

Organic semiconductors are inherently soft materials, making them ideal for applications with innovative form factors which are not easily achievable with rigid inorganic materials. Some applications include flexible, conformable, and foldable displays and sensors [6, 17, 73, 74]. This mechanical flexibility of organic semiconductors also facilitates the development of stretchable sensors and conformable medical devices that can adhere closely to the human body, providing continuous health monitoring and diagnostic capabilities with greater comfort and accuracy. Furthermore, the organic electronics enables mechanical stability for large-area applications when exposed to conditions where durability and robustness are critical for adoption [75, 76].

A prominent biophotonic application leveraging developments in organic optoelectronics is the pulse oximeter. Pulse oximeters are critical medical devices used in clinical settings, emergency medicine, and home healthcare to assess respiratory function and overall patient health. The conventional method of pulse oximetry utilizes inorganic light-emitting diodes (LEDs) and a photodiode (PD) to non-invasively measure pulse rate and arterial blood oxygen saturation. This non-invasive optical technique is called photophethysmography (PPG), where changes in blood are measured through variations in light absorption at the skin's surface. LEDs emit light through tissue, which is then reflected or transmitted by the skin and detected by the photodiode, providing data on oxygenated and deoxygenated hemoglobin levels. Finger pulse oximeters are commonly used at home and in clinical settings, however, the device is often constrained by the bulkiness and rigidity of the system, making them uncomfortable and inconvenient to use for long periods. This is in part due to the rigid inorganic devices used. Furthermore, extended periods of continuous monitoring will require a connection to a constant power supply, making the device even more cumbersome and less convenient for long-term use.

On the other hand, organic-based devices offer several potential advantages, including enhanced flexibility, reduced manufacturing costs, and compatibility with wearable and skin-like electronics. Using organic LEDs (OLEDs) and photodiodes (OPDs) enable the integration of a lightweight, flexible, and low-cost PPG sensor. Significant strides have been made in developing and demonstrating the feasibility of organic-based sensors. Lochner et al. (2014) pioneered the first all-organic PPG sensor using solution-processed OLEDs and OPDs [77]. Following this, developments in PPG sensors have included the use of higher performance semiconducting materials, enhanced flexibility, self-powered PPGs, and wireless capabilities [78–84]. These contributions highlight a shift from bulkier electronic interfaces towards a more durable and miniaturized wearable system.

Another significant advancement in organic-based PPG sensors was demonstrated by Khan et al. (2018) where a large-area 2D oxygenation mapping system was developed [85]. The flexible and printed electronic system is achieved by printing and integrating arrays of OLEDs and OPDs stacked atop one another. The devices are fabricated on flexible plastic substrates, enabling a lightweight sensor array that is comfortable to wear while also increasing signal-to-noise ratio by improving the fidelity of the sensor-skin interface.

These reports demonstrate strong interest in implementing organic devices in medical sensors. However, a major challenge in realizing an integrated health monitoring device with organic electronics is the high driving voltages and larger parasitic capacitances of OLEDs and OPDs. This can significantly increase the power consumption of the pulse oximeter, diminishing the practicality of using organic-based devices in medical applications. Reducing sampling rates or driving voltages of organic devices can help to reduce the power consumed, however, at the cost of sensor accuracy. This is not ideal for medical sensing applications where continuous and accurate monitoring of vital signs is critical. To address these challenges while leveraging the unique properties of organic-based PPG sensors, the system architecture must be adapted to meet the specific needs of organic devices. Chapter 2 demonstrates steps towards an improved system for organic-based PPG sensors with a custom integrated circuit. Specifically designed for use with organic devices, this work contributes a method for decreasing power consumption while maintaining accuracy. Overall, the development of organic-based PPG sensors exemplifies advantages of organic electronic devices in healthcare applications, facilitated by solution processing for scalable and cost-effective manufacturing.

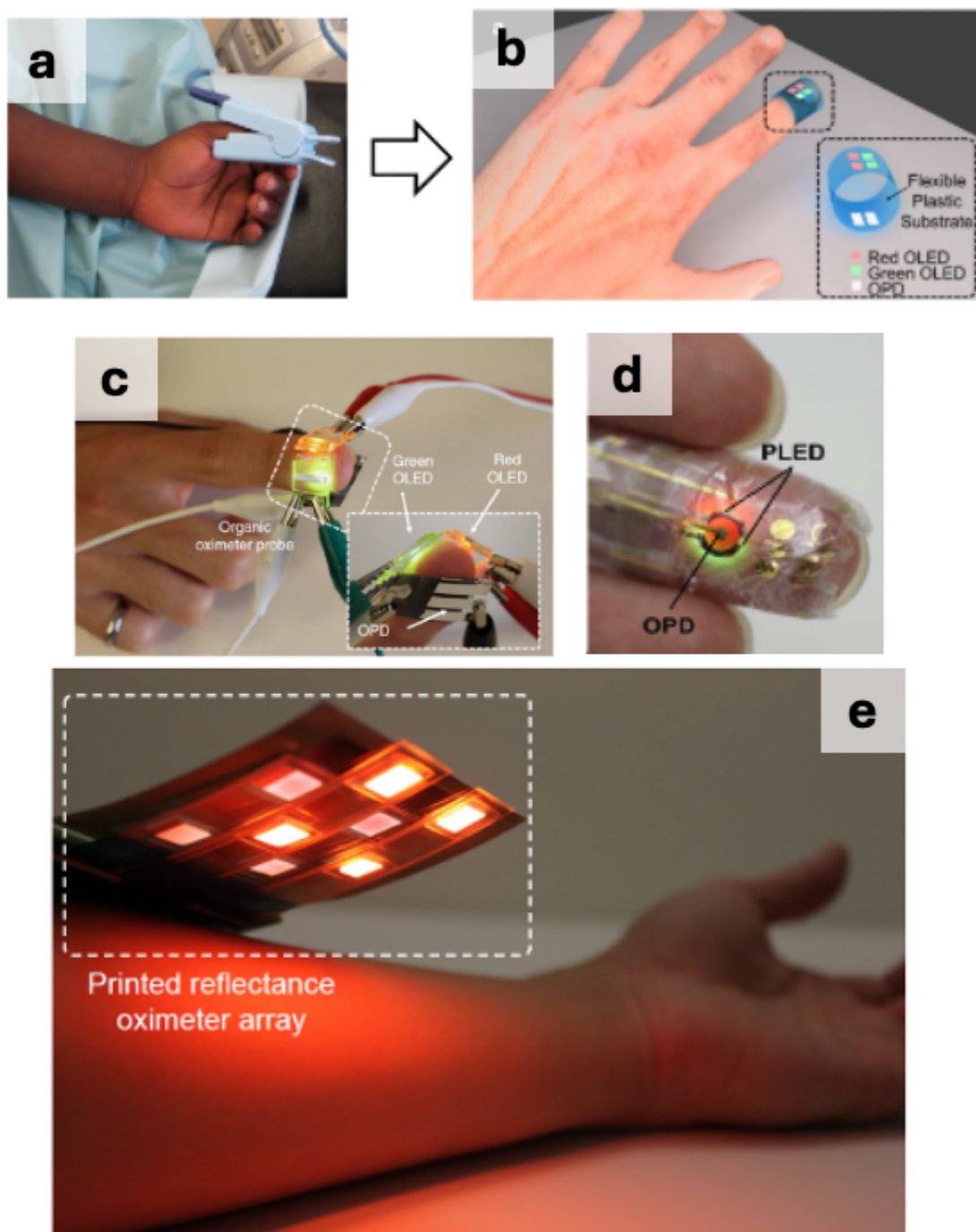


Figure 1.13: Images demonstrating the progress in pulse oximeter technologies. The images shown are: a) rigid and bulky commercial pulse oximeter b) concept art of a flexible organic-based pulse oximeter, c) PPG sensors based on solution-processed organic devices, d) a solution-processed PPG sensor fabricated on ultraflexible d) a printed reflectance oximeter array [77, 85, 86].

1.3 Fabrication Methods

Key to enabling the unique applications of organic electronics is the solution solubility of organic semiconductors. Dissolution of small molecule and polymer semiconducting materials into homogeneous inks enable the deposition of electronics as thin-films. While conventional electronics manufacturing require vacuum deposition techniques with high thermal budgets, solution-processed organic electronics can be fabricated using low processing temperatures, on a variety of substrates, and with scalable manufacturing techniques.

Various solution-based techniques have been utilized to deposit layers of polymer semiconductors, with spin coating emerging as the predominant method in research settings [12, 14, 87]. Spin-coating is convenient for producing uniform and reproducible films on flat substrates, allowing tunability of film thicknesses through adjustments in spin speed and solution viscosity [88, 89]. Spin-coating is also a critical method used in commercial fabrication of nano- and microelectronics during photolithography. In terms of operation, spin coating can be broken down into several steps. Initially, the solution is applied onto the substrate, either through dynamic or static spin coating methods, allowing centrifugal motion to spread it evenly. As the substrate reaches its maximum rotational speed, excess solution is expelled. The fluid begins to thin, primarily through solvent evaporation, influenced by factors such as volatility and ambient conditions. These steps can be seen in Figure 1.14. In general, the thickness of a spin coated film is inversely proportional to the square root of the spin speed seen in equation 1.21 where ω is spin speed and h_f is final film thickness. The film's exact thickness is influenced by factors such as material concentration, solvent evaporation rate, solvent viscosity, temperature, and humidity. Thus, spin thickness curves are usually determined empirically with ellipsometry or surface profilometry.

$$h_f \propto \frac{1}{\sqrt{\omega}} \quad (1.21)$$

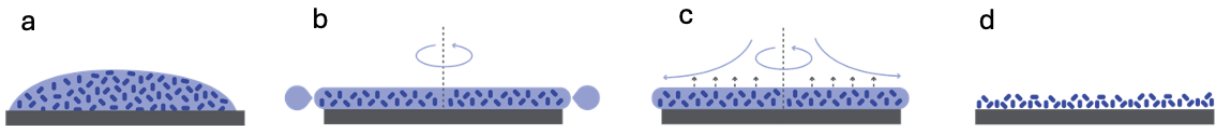


Figure 1.14: Illustration of spin coating steps using a static dispense method. a) Solution deposited on the surface of the substrate b) Rotation begins and excess solution is expelled c) solvent evaporation and film solidification d) final film is formed. Figure adapted from Ossila [90].

Although spin-coating is a well-controlled and established solution processing method, it poses a drawback in its inefficient material usage [91]. During the spin-coating process, a majority of the starting material is spun off the substrate, leaving only a thin wet film behind. In addition, spin-coated films often require subtractive post-processing steps to develop desired patterns [92, 93]. For instance, spin-coating is often followed by etching steps to develop 2D patterns. On the other hand, additive manufacturing deposits material directly where it is needed. Additive techniques include inkjet printing, screen printing, gravure printing, doctor blade coating, slot dye coating and spray coating. Each of these methods offers unique advantages in terms of precision, material usage, and suitability for different applications [13, 20, 94]. The characteristics of the solution being deposited will limit the available fabrication techniques [95–98]. A comparison of various printing techniques can be seen in Figure 1.15. Solution viscosity is a critical parameter that impacts the deposition capabilities and may even limit the feasibility of some techniques [87]. For instance, inkjet printing and spray coating techniques will require lower viscosity solutions to prevent clogging and proper ejection [99–101]. On the other hand, blade coating tolerates a larger range of viscosities from low viscosity organic inks to higher viscosity metallic pastes [102, 103]. Where the solution may limit the choice of printing technique, the printing technique also limits the resulting film deposition speed and resolution. For instance, inkjet printing is commonly used to print high resolution features, however, this comes at the cost of printing speed and scalability [104, 105]. On the other hand, blade-coating is typically used to blanket coat thin films and is better suited for scaling to larger areas. A wide variety of organic devices from blade-coated OLEDs to inkjet printed OPVs to screen-printed electrochemical transistors have been fabricated with printing techniques and are shown in Figure 1.16.

Organic optoelectronic solutions exhibit low viscosities between 1 to 100 cP, making them well suited for doctor blade coating. A variety of devices have been blade-coated including phototransistors, light-emitting diodes, photodiodes, and photovoltaics [49, 107–113]. A primary advantage of blade coating over similar printing techniques is the simplicity of printing parameters. Blade-coating involves spreading solution over a substrate using a blade at a designated blade height and speed. In contrast, techniques such as inkjet printing and slot-die coating require intricate optimization of droplet formation and deposition or the management of complex fluid dynamics. Blade coating offers a straightforward and reliable approach to depositing thin films at scale. Additionally, films can be deposited with sequential blade-coating steps, enabling the fabrication of multilayered films necessary for applications like organic optoelectronic devices.

However, blade coating also possess drawbacks in terms of 2D patterning. Designed primarily for large-area, uniform coatings, blade coating is not inherently suited for patterning films. While stencils can be used to create patterns, this method works best with high-viscosity solutions that adhere well to the substrate after deposition [114–116]. Low-viscosity solutions, on the other hand, tend to spread before the film dries, leading to poor pattern definition and control. For the same reasons, realizing sharp and well-defined edges

Printing properties	Inkjet Printing	Screen Printing	Gravure Printing	Blade Coating	Spray Coating
Ink viscosity	5 – 50 cP	500 – 5000 cP	10 – 1000 cP	<100 cP	10 – 100 cP
Critical linewidth	30 – 70 μm	50 – 150 μm	5 – 100 μm	–	50 – 150 μm
Film thickness	0.1 – 1 μm	5 – 100 μm	0.1 – 1 μm	0.1 – 1 μm	0.5 – 1 μm
Film roughness	Low	High	Low	Low	Medium
Printing speed	0.01 – 0.1 m s^{-1}	0.1 – 1 m s^{-1}	0.1 – 10 m s^{-1}	0.01 – 1 m s^{-1}	0.1 – 1 m s^{-1}
2D patterning	Yes	Yes	Yes	No	Yes
Large-area scalability	Limited	Yes	Yes	Yes	Limited
Design flexibility	High	Low	Low	Medium	Medium

Figure 1.15: Side views of common printing techniques and a comparison of their associated solution, film, and printing characteristics. Figure from Pierre (2017) [106].

in blade-coated patterns can be challenging depending on the solution. However, surface energy patterning (SEP) has shown to be an effective method for patterning blade-coated films [117]. This method leverages differences in surface energies on the substrate to guide the deposition and spreading of the coated solution, enabling pattern formation without the need for stencil masks. Blade coating on a surface energy patterned substrate has been demonstrated in the fabrication of printed organic transistors, organic light emitting diodes, and organic photodiodes [85, 107, 108, 110]. The use of blade coating on SEP substrates enables a facile and scalable printing method without the need for costly engraved cylinders such as those used in gravure printing. The advancement of this technique for the fabrication of blade-coated multi-functional organic optoelectronic devices is the subject of Chapter 3. Using a scalable and low-cost blade coating technique, this work demonstrates important steps in reducing the fabrication complexity of optical systems while ensuring high performance of device printed.

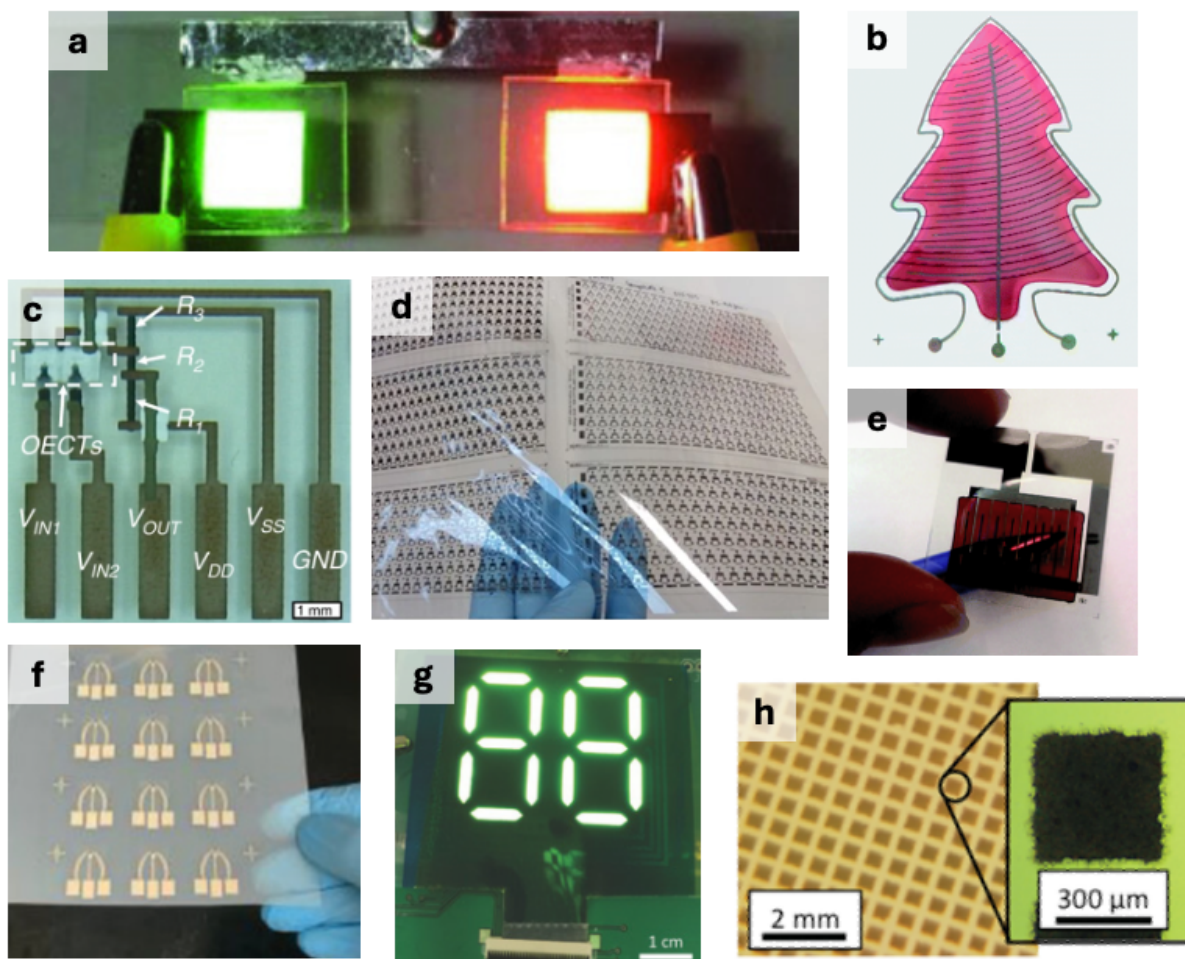


Figure 1.16: Examples of organic devices fabricated with various printing techniques. Images include: a) multicolored blade-coated OLEDs, b) fully inkjet printed OPV Christmas tree, c) screen-printed organic electrochemical transistor circuits, d) all-inkjet-printed TFT array, e) semitransparent inkjet printed organic solar cell f) screen-printed organic electrochemical transistor sensors, g) a 7-segment display based on blade-coated OLEDs, and h) printed organic photodiode arrays [101, 109, 110, 118–120] .

1.4 Materials and Solvents

While scalable printing techniques help to address the economic prospect of electronic manufacturing, another critical consideration for the commercial viability of organic electronics is the environmental impacts of the materials used in the process. Sustainable practices to reduce overall environmental impact of electronic manufacturing can be achieved by reducing toxicity of materials and solvents, improving stability and longevity of devices, and utilizing renewable resources when possible. The use of additive printing techniques helps to reduce material waste by depositing precise amounts of material only where needed. However, the solutions used in printing organic electronics can still be hazardous. Developing and utilizing non-toxic materials and solvents are crucial for moving towards greener and sustainable practices.

Organic materials are inherently less toxic compared to some hybrid or inorganic materials. For instance, non-organic solar cell materials often utilize high heavy metals with unstable bonds, such as lead in perovskite solar cells, which pose significant environmental and health risks [58, 121]. These heavy metals can leach into the environment during manufacturing, usage, and disposal, posing long-term health hazards to humans and wildlife. In contrast, organic semiconductors, carbon-based materials, are generally considered to be less hazardous and environmentally friendly. Without toxic metals, organic electronics are typically safer to produce, handle, and dispose of [19, 122, 123]. This environmental benefit is crucial as industries move towards greener technologies and sustainable practices.

However, a major challenge still remains in organic semiconductor processing: reliance on toxic solvents. Organic solvents play a crucial role in the fabrication of organic semiconductor devices. Solution processed organic materials require proper functional solvents to facilitate proper dissolution, allowing the deposition of thin films and help in achieving the desired morphology and crystallinity of the active layer [124, 125]. In addition to solubility of the organic semiconductor material, solvent choice also depends on the solvent volatility. The host solvent of an organic semiconductor blend, along with the semiconductor properties (π stacking, crystallinity, etc.), will be affected by the evaporation rate of the deposited film. Processing and post-processing parameters can be used to accelerate drying and realize ideal film morphologies [124, 126, 127].

Organic semiconductors contain a high content of aromatic subunits within their chemical structures, making halogenated and aromatic solvents the most compatible for dissolution [78, 128, 129]. This has led to widespread use of solvents such as chloroform, chlorobenzene, toluene, and xylene in record performing organic devices [38, 52, 130]. However, scaling the deposition of organic electronics when highly toxic solvents are used is a growing concern. For instance, chlorinated solvents, although effective in achieving high-quality organic thin films and commonly used in high performance organic solar cells, are often associated with environmental and health concerns due to their toxicity [131–134]. Thus, a growing focus in

organic electronics research is aimed to address the impact of solvent selection on electronics manufacturing. There are different approaches to realizing green solvent-processable organic electronic devices. The first is a material modification method, which involves tailoring the solubility of organic molecules and polymers by modifying their structure while maintaining their essential characteristics. The second is the solvent selection method, testing alternative solvents with well established semiconductor materials.

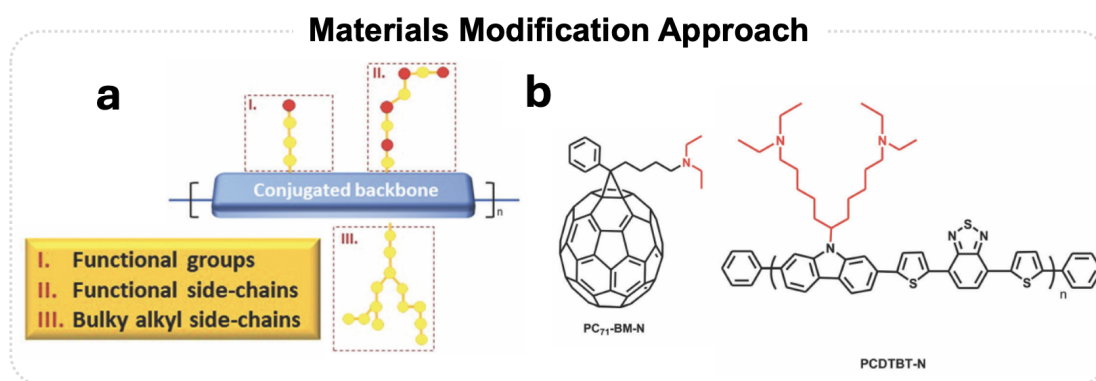


Figure 1.17: Illustration of materials design strategy for green solvent processable organic semiconductors. a) Three widely used approaches are to attach functional side groups, functional side-chains or bulky alkyl side-chains. b) Cao et al. functionalized the alkyl chains of both PCDTBT and PC₇₁BM with a terminal tertiary amino group, to obtain a butanol/acetic acid soluble donor PCDTBT-N and acceptor PC₇₁BM-N. Adapted from Campana et al. (2020) and Duan et al. (2013) [135, 136].

The material modification of organic semiconductor materials can be done by adding functional groups, functional side-chains, or bulky alkyl side-chains as seen in Figure 1.17. An example of a function group addition is attaching ionic terminal groups on alkyl chains to enable higher solubility in more ionic or hydrophilic solvents such as water or alcohol [137]. However, this modification may lower device efficiencies due to the ionic terminal groups' potential to charge traps and act as quenching sites. Another strategy is to attach non-ionic but highly polar terminal groups to conjugated polymer backbones, achieving slightly improved device performances [138, 139]. Bulky alkyl side groups can also enhance the solubility of conjugated systems in greener organic solvents [19, 139]. However, this is at the cost of molecular packing and consequently the device electronic characteristics. These material design approaches are also applied to small molecule acceptors. To start, popular fullerene acceptors are known to have low solubility in non-halogenated solvents [139]. Some groups have demonstrated modifications on PCBM acceptors, demonstrating highly soluble fullerene derivatives in greener solvents such as anisole or 2-methyl-tetrahydrofuran [140, 141]. However, these films also tended to exhibit lower crystallinity than chlorinated-solvent

processed films. Therefore, although there is promise for design approaches to enable organic semiconductors soluble in greener solvents, recent reports show that material modifications typically yield lower device performances than solvent replacement strategies [135].

Solvent replacement approaches tackle the reliance of hazardous solvents used in organic electronics by directly replacing them with greener solvent alternatives. A graphical abstract of the solvent replacement approach is given in Figure 1.18. The primary challenge in this approach is finding a suitable solvent that maintains the desired morphology and microstructure of the thin film [142]. High solvent volatility can lead to rapid evaporation and may not provide sufficient time for phase separation in solution blends. Conversely, low volatility solvents can result in prolonged drying times, leading to undesired coalescing of pure domains, reducing necessary interfacial junctions. Another major limitation to the realization of green solvent processed optoelectronic devices is the low solubilities of organic semiconductors. It is generally known that the host solvent should enable sufficient concentrations (≥ 10 mg/mL) for homogeneous dissolution, good molecular packing, and high viscosity for film thickness tuning [139]. The balance between these critical parameters is shown in Figure 1.18b, where Lee et al. (2020) highlights an optimal intersection between boiling point and solubility. The solubility plotted is based on Hansen Solubility Parameters (HSPs), a theoretical physical parameter used to assess solvent similarities. This theory and its use in solvent selection is discussed in more detail in future Chapters [143–146]. Finally, the solvent replacement approach considers the toxicity of the solvent as shown in Figure 1.18 where common solvents broken down into chemical categories. Generally, chemicals such as alcohols and esters may be preferred due to their lack of toxicities, however, they are often not compatible for dissolving conjugated polymers used in organic electronics. Another approach is to form surfactant-stabilized nanoparticle dispersions to deposit a photoactive layer from aqueous solutions [147–150]. However, this approach is limited by the ability of donor and acceptors to form suitable nanoparticles for optimal film morphology and the addition of surfactants that increase charge recombination [76].

There is a balance between the critical parameters: toxicity, solubility, boiling point. In addition, film processing techniques can play a crucial role in overcoming some of the limitations associated with the solvent's properties. Solution blends can be optimized to increase solution concentrations and post-annealing can be used to accelerate drying of films deposited from low volatility greener solvents. By optimizing film processing methods, it is possible to achieve high-quality films when using greener solvents. Investigation and critical optimization steps for using greener solvents for organic solar cells is discussed in further detail in Chapters 4 and 5.

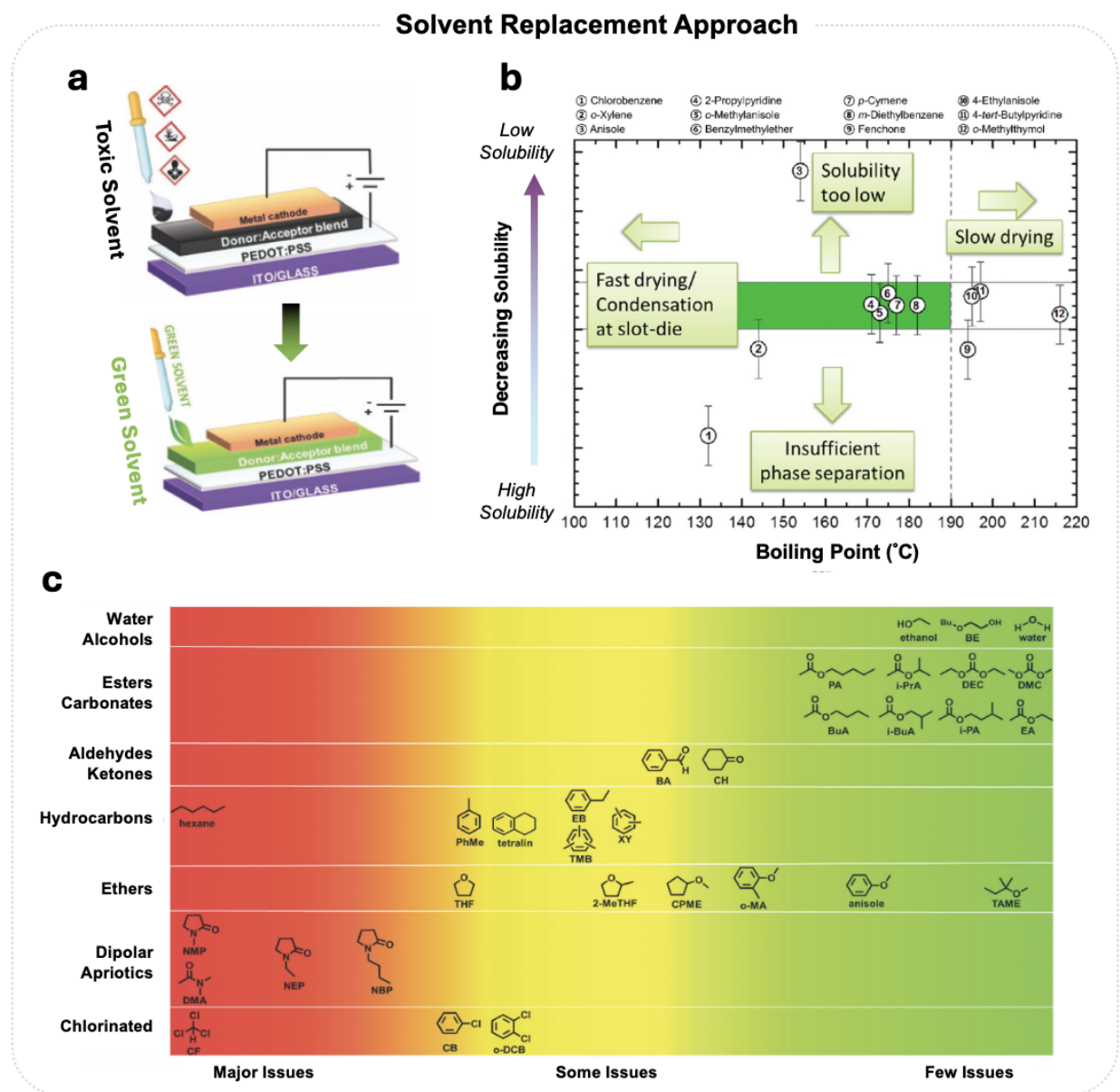


Figure 1.18: Solvent replacement approach and considerations for processing organic semiconductors with green solvents. a) Illustration of how the toxic solvent in the donor:acceptor blend is replaced with a green solvent. b) Plot depicting the solubility of P3HT in various solvents as a function of the solvent boiling point. Solvents inside the green box, which is surrounded by three boundary conditions, are considered suitable for achieving homogeneous films during the large-area roll-to-roll coating. c) Ranking of solvents investigated for organic semiconductor processing based on the overall greenness. Adapted from Campana et al. (2020) and Lee et al. (2020) [19, 135].

1.5 Dissertation Organization

This thesis provides critical steps towards eco-friendly and scalable organic optoelectronic sensors. First, integration of organic biophotonic sensors and a custom designed integrated circuit is demonstrated in a wearable pulse oximeter. Then, inspired by the needs of optoelectronic applications where multiple devices are used, a printing technique for simultaneous deposition of multi-functional films is optimized. Finally, to address the environmental impacts of manufacturing large-area devices, green solvent processing of organic solar cells are investigated.

Chapter 2 details the challenges with realizing wearable sensors using organic devices. LEDs and photodiodes are active components, requiring voltage biases for optimum performance. To demonstrate the feasibility of organic-based sensors in medical applications, systems must be adapted to serve the needs of the sensors used. First, the principles of pulse oximetry and the fabrication of suitable OLEDs and OPDs are shown. The chapter then discusses testing and validation of a custom sensor IC developed for organic-based PPG sensors. A sparse sampling method is validated for further decreasing power consumption while maintaining accurate medical readings.

Motivated by the need of both light emitting and light detecting devices in PPG sensors, chapter 3 demonstrates the use of surface energy patterning for the fabrication of multi-functional films. This chapter first details the fabrication technique for simultaneous optimization of blade-coated OLED and OPDs on large-area and flexible substrates. Careful consideration of contact angles of the print surfaces are critical to enable deposition of distinct films. To optimize desired characteristics of both devices, film thicknesses are optimized by tuning solution active layer concentrations.

Chapter 4 addresses the environmental impact of large-area fabrication of organic devices. Organic solvents are necessary for solution processing of organic semiconductors. Common organic solvents used in literature are first discussed. Resources for defining and categorizing solvent safety and toxicities (Global Harmonized System, industry-relevant solvent guides) are discussed in detail. Finally, Hansen Solubility Theory is presented as a theoretical foundation for selecting suitable greener solvent alternatives.

Building on the previous discussion, chapter 5 demonstrates a method that considers greener and more environmentally friendly solvents for the fabrication of organic solar cells. First, the solubility of a combination of photoabsorbing materials and greener solvents are evaluated. Analyzing the concentrations of prepared solutions, a single solvent is chosen to compare its substitution of a chlorinated solvent. Drying times of spin-coated and printed films are analyzed to understand the impact of the greener solvent on film formation. Optimizing the solution formulation and post-processing conditions, spin-coated solar cells are fabricated with a greener solvent. Blade-coated organic solar cells are fabricated with

the greener solvent, demonstrating comparable device power conversion efficiencies.

Chapter 6 concludes this thesis and discusses future work. The use of optically transparent plastic substrates with organic optoelectronics shown in Chapter 2 and 3 enable the possibility of integrating the PPG sensor with other flexible medical on-skin sensors. An integrated impedance and optoelectronic sensors for wound monitoring and stimulation is shown. Next, improvements for greener solvent processing is discussed. Mixing a new combination of more soluble donors and acceptors in solution blends could increase the efficiencies shown in the previous chapter. The durability and operational lifetimes of organic electronics are crucial to improving their cost-effectiveness and reducing their environmental impacts of electronic waste. Device encapsulation is a critical technology used to prevent degradation and extend operational lifetimes of organic devices. Results utilizing a nanocomposite encapsulation for oxygen and moisture barrier is presented.

Chapter 2

Organic Optoelectronic Sensors

2.1 Overview

Health monitoring devices require low power sensors with extended battery life for continuous monitoring. The operating system must meet the demands of the sensor, as well as power used for data analysis and communication. For organic-based devices, additional design is necessary to address the higher driving voltage and increased parasitic capacitances of organic devices [151, 152]. The parasitic capacitance of photodiodes can impact the input referred noise of the transimpedance amplifier by attenuating the feedback factor as the frequency increases [153, 154]. Organic photodiodes can exhibit larger capacitances of up to 10 nF compared to silicon photodiodes with 100 nF. Similarly, the higher driving required for organic LEDs restricts battery life. The duty cycle of the components can be adjusted to reduce power consumption, but need to be validated to avoid compromising the reliability and accuracy of medical readings. Off-the-shelf components reduce cost and improve simplicity of designs, however, at the cost of power usage [151]. To fully leverage the use of organic-based PPG sensors in medical applications, the system must be tailored for the specific needs of organic devices. The following chapter demonstrates the testing and validation of a custom sensor IC for PPG sensing with organic devices. This work is a critical step towards compact and efficient medical monitoring with flexible and lightweight sensors.

2.2 Pulse Oximetry

Pulse oximetry is a technique for determining oxygen saturation utilizing light absorption of oxygenated and deoxygenated blood at two different wavelengths. Conventional pulse oximeters use an optoelectronic sensor with inorganic LEDs and a photodiode (PD) placed on opposite sides of a finger to non-invasively measure pulse rate and arterial blood oxygen saturation. This setup is effective, however, bulky and rigid. A combination of organic-based LEDs and PDs can be manufactured via solution-processable techniques and

integrated to form a pulse oximeter system. Organic semiconductors offer large-area roll-to-roll manufacturing, flexibility, and solution processing advantages, making them especially attractive for medical sensors.

The measurement used is known as photoplethysmography (PPG), wherein the absorption of light within the blood is assessed [155, 156]. This method relies on the understanding that functional hemoglobin transports oxygen through the bloodstream, and by optically quantifying the levels of oxyhemoglobin (HbO_2) and deoxy-hemoglobin (Hb), the oxygen saturation (SO_2) in tissues can be estimated. SpO_2 depends on the relative concentration of oxygenated versus deoxygenated hemoglobin, and hence, requires information at two different light wavelengths. As light passes through the tissue, it is attenuated by different elements, and this attenuation is described by the extinction coefficient. As illustrated in figure 2.1, the molar extinction coefficients of HbO_2 and Hb exhibit significant variations across wavelengths. As such green, red, or near-infrared (NIR) light sources are often employed in medical sensors and fitness watches. Notably, given the differences in molar extinction coefficients and their ability to penetrate human tissues, the combination of red and NIR wavelengths prove to be more effective. The value of SpO_2 is computed based on the ratio of the AC component over the DC component of red and IR PPG waveforms. The calculations are shown in 2.1 and 2.2 where ε is the extinction coefficient of light at red or IR wavelength through oxygenated or deoxygenated hemoglobin [156]. To compute SpO_2 , only the peak and valley (PAV) values of the PPG signals are needed in the two wavelengths. It is therefore possible to only sample the signal PAVs and, as a result, save power.

$$R_{OS} = \frac{I_{AC,Red}}{I_{AC,IR}} \cdot \frac{I_{DC,Red}}{I_{DC,IR}} \quad (2.1)$$

$$SpO_2 = \frac{\varepsilon_{Hb,Red} - \varepsilon_{Hb,IR} \cdot R_{OS}}{\varepsilon_{Hb,Red} - \varepsilon_{HbO_2,Red} + [\varepsilon_{Hb,IR} - \varepsilon_{HbO_2,IR}] \cdot R_{OS}} \quad (2.2)$$

Pulse oximeters operate in two modes relating to the relative positioning of PD and LED: transmission mode and reflection mode as seen in Figure 2.1. Transmission mode requires transmission through tissues and are often measured through extremities such as the fingers (1). Commercial PPG systems used in clinical settings employ transmission mode sensors measured on the index finger. Reflection mode PPG measures light back-scattered or reflected from tissue, bone, or blood vessels (2). Reflection mode is more flexible in that the sensor can ideally be placed anywhere on the body.

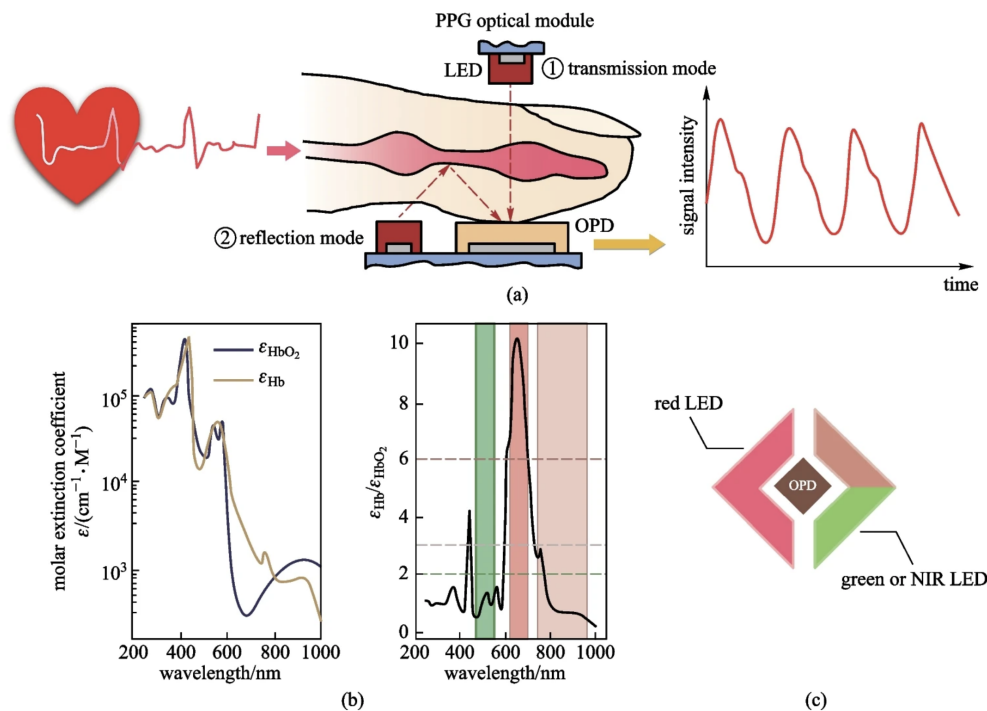


Figure 2.1: Monitoring heart rate and blood oxygen saturation by PPG. a) Working principle of PPG: transmission and reflection mode. b) Molar extinction coefficients of Hb and HbO₂ at different wavelengths. c) Schematic diagram of an oximetry system containing photodiode and two light-emitting diodes. Figure from Shan et al. (2022) [48].

2.3 Organic-based PPG Sensors

The organic devices used to test iterations of this custom IC system were fabricated with both printing and spin-coating techniques [77, 110, 151]. Device areas were varied to increase light output and emission coverage. Broad spectrum absorbing OPDs were fabricated similarly.

Illustrations of the OLED device design is shown in Figure 2.2a and b. The desired emission color can be tuned based on blend used in the the emissive material. The green OLEDs were fabricated from a blend of poly(9,9-dioctylfluorene-co-(4-butylphenyl)-diphenylamine) (TFB) and poly((9,9-dioctylfluorene-2,7-diyl)-alt-(2,1,3-benzothiadiazole-4,8-diyl)) (F8BT). The red OLED was fabricated from a tri-blend blend of TFB, F8BT and poly((9,9-dioctylfluorene-2,7-diyl)-alt-(4,7-bis(3-hexylthiophene-5-yl)-2,1,3-benzothiadiazole)-2',2'-diyl) (TBT). The compositions are 1:9 TFB:F8BT and 25:70:5 TFB:F8BT:TBT dissolved in o-xylene for green and red blends, respectively. The NIR OLEDs were fabricated from a proprietary blend provided by collaborators at Cambridge

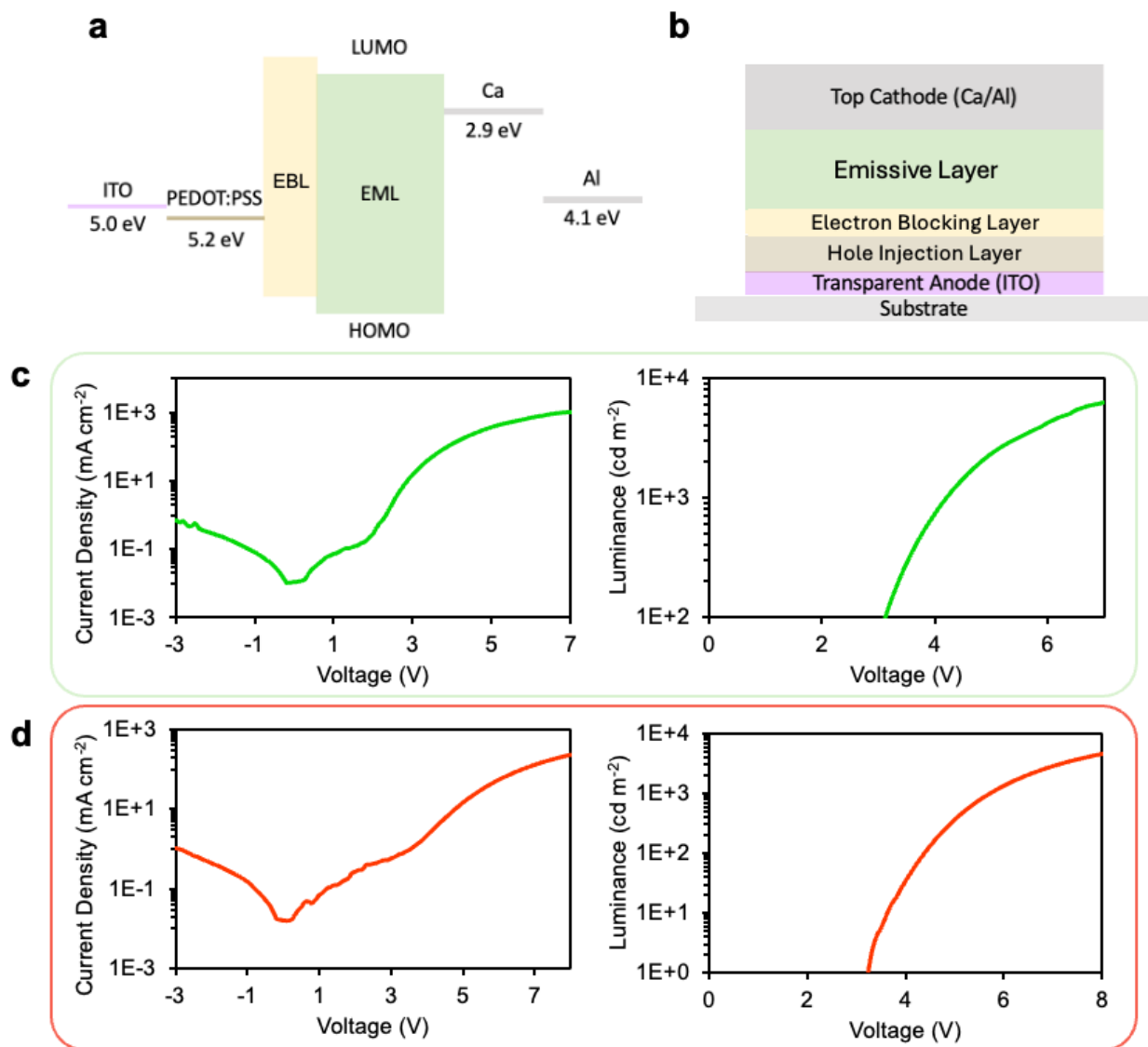


Figure 2.2: Illustrations of OLED devices and example device characteristics. a) Band diagram of OLED devices fabricated. b) Device film stack of OLED devices fabricated. Emissive layer materials chosen based on the desired emission color (green, red, etc.). c) Representative current density versus voltage and luminance versus voltage characteristics of green OLEDs. d) Representative current density versus voltage and luminance versus voltage characteristics of red OLEDs.

Display Technology (Sumitomo Chemical Group). The solution is prepared by dissolving the NIR materials in toluene. The OLED device stacks utilize indium tin-oxide (ITO) as the

transparent anode, Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) as the hole injection layer, TFB as the electron blocking layer, and a calcium/aluminum (Ca/Al) top cathode. Example device characteristics of green and red OLEDs are shown in Figure 2.2 with turn-on voltages of 2.7 and 3.6 V, respectively.

The performance of OLED and OPD devices should be characterized to ensure compatibility with PPG applications. OLEDs should emit light at wavelengths where there is a difference in molar extinction coefficient of oxygenated and deoxygenated-hemoglobin. Examples of spin-coated green, red, and NIR OLED devices are shown in Figure 2.3. The peak emission wavelengths for the OLEDs were 520, 615 and 725 nm for green, red, and NIR OLEDs respectively. Green and NIR OLEDs exhibit comparable differences in molar extinction coefficients, while red exhibits the highest (as seen in Figure 2.1b).

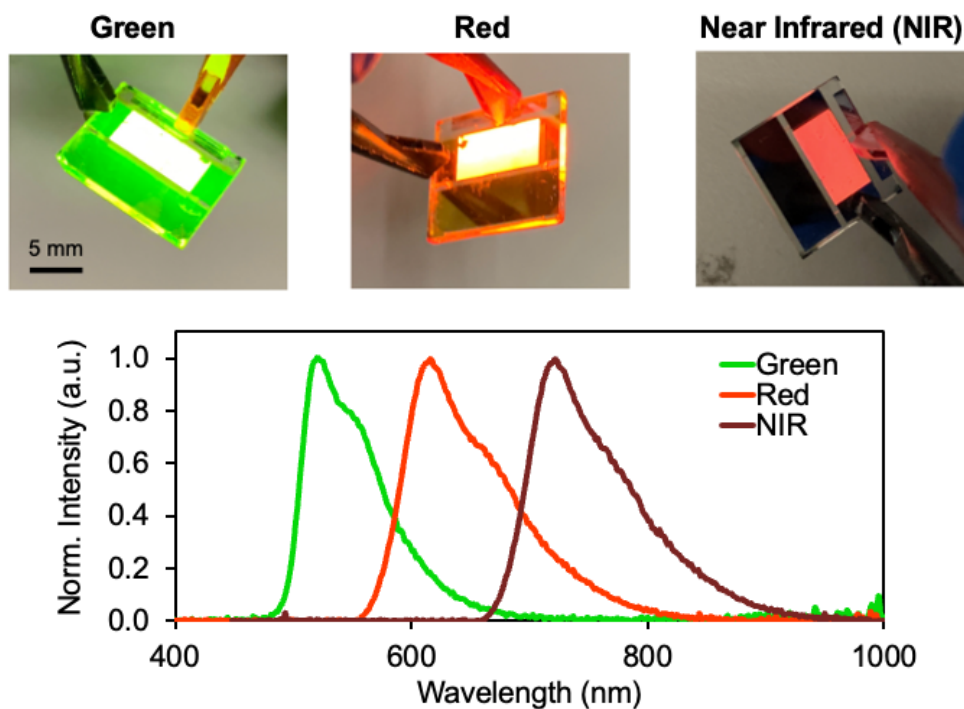


Figure 2.3: Images of spin-coated green, red, and NIR OLEDs captured by a smart phone camera. Devices were used for testing iterations of the custom IC.

Similarly, for sensing PPG signals, the OPDs should exhibit high EQE at the peak OLED emission wavelengths. A high EQE enables a photocurrent in response to reflection or transmission of light signal from the skin. Here, the OPDs consisted of a device stack with ITO as the transparent electrode, PEDOT:PSS as the hole injection layer, a photoabsorbing layer, and aluminum as the top electrode. As seen in Figure 2.4, the OPD exhibits broad

absorption over visible and NIR wavelengths, compatible with the emission of fabricated OLEDs represented by the three colored bands. The OPDs exhibit high EQEs of roughly 40% at zero bias. The photoabsorbing layer consists of a blend of a proprietary donor material (Cambridge Display Technology) and PC₇₁BM.

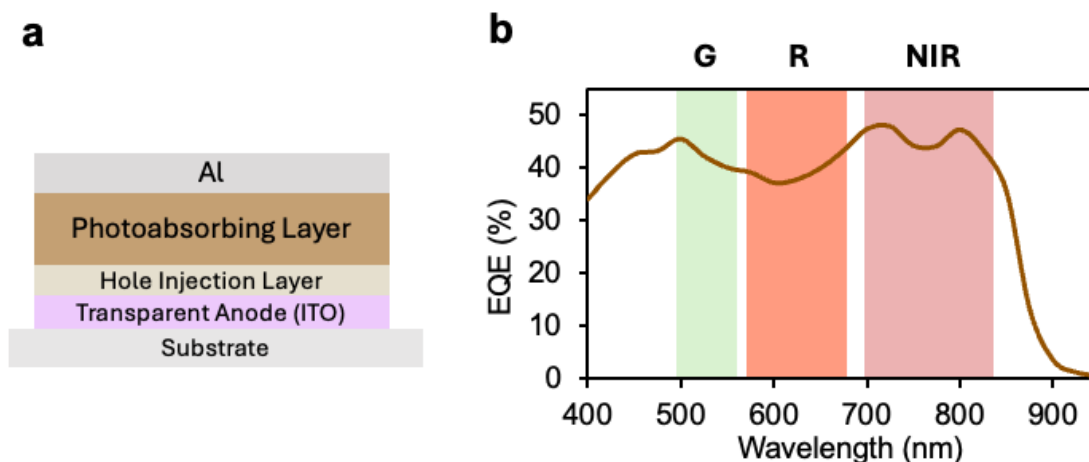


Figure 2.4: a) Illustration of device film stack of OPD devices fabricated. b) EQE measured of OPDs fabricated with three colored bands representing emissions of OLEDs fabricated. OPD performance at zero bias demonstrates its compatibility for pulse oximetry measurements.

2.4 Sensor Interfacing

The organic pulse oximetry sensor composed of two different colored OLEDs and a OPD. During measurement, the OLED is electrically driven while the OPD signals are measured and transferred for calculations and analysis. For a robust and reliable testing set up, a custom printed circuit board (PCB) was designed. Silver traces were printed via stencil printing on flexible plastic substrates and Al tape and silver paste were applied to electrically connect to the traces and individual devices. The silver traces were secured with flat flexible cable (FFC) connectors during testing. Vias connecting the FFC and bottom pins on the opposite side of the PCB allowed for connection to external circuitry for OLED driving and OPD readout. An example of the assembly can be seen in the images in Figure 2.5. This testing set up allowed for modularity in testing both transmission and reflectance mode pulse oximetry. A schematic for transmission measurements can be seen in Figure 2.6 where the OPD and OLEDs are confined via separate boards. Additional foam padding is used to block out ambient lighting and interference during measurement.

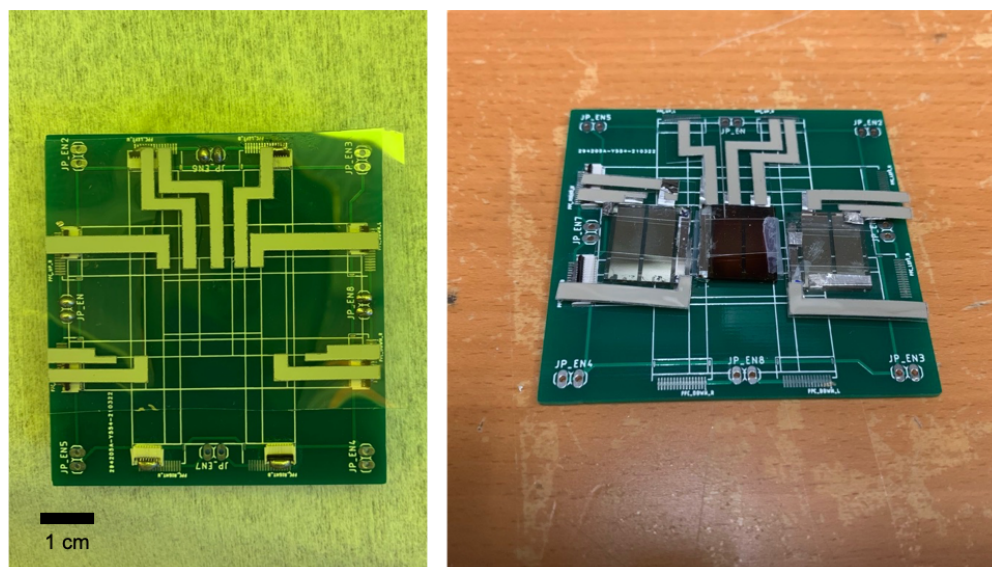


Figure 2.5: Images of an example configuration to test organic PPG sensors. (Left) Stencil-printed silver traces on PEN were used to make anode and cathode connections to the organic devices. (Right) Image of a reflectance mode configuration with the OPD and two OLEDs connected to the FFC for power and readout via the stencil printed traces.

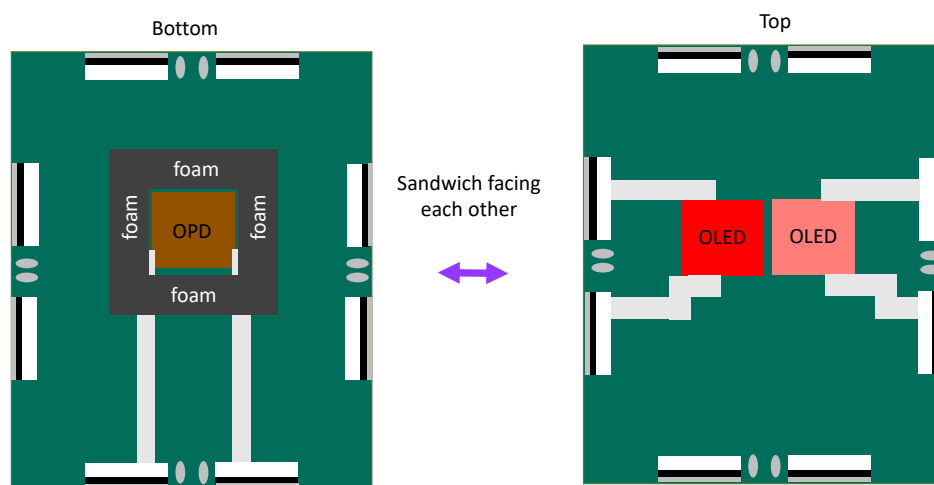


Figure 2.6: Schematic of devices and boards configured for transmission measurement testing. The OLED devices are secured to one board with FFC connectors. The OPD is secured to another with additional foam padding to reduce ambient light and interference.

2.5 Sensor Integrated Circuit

The following section highlights a collaborative work led by Sina Faraji Alamouti in the developments of a sensor integrated circuit (IC) for continuous SpO_2 and HR monitoring using organic optoelectronics [153, 157, 158]. Figure 2.7 shows a graphical abstract of developing a sensor IC targeted for PPG sensing. The operation of a pulse oximeter depends on LEDs being driven sequentially while reflected or transmitted light is received by the photodiode. Induced photocurrent makes up the PPG signal. The input DC component is subtracted using differential current DACs (I-DACs) in order to relax the dynamic range requirements. The remaining AC component is then amplified, filtered, and digitized through the readout chain. Timing between LED driving and photocurrent measurements are controlled by the timing unit. The on-chip digital back-end then computes the remaining processing and analysis.

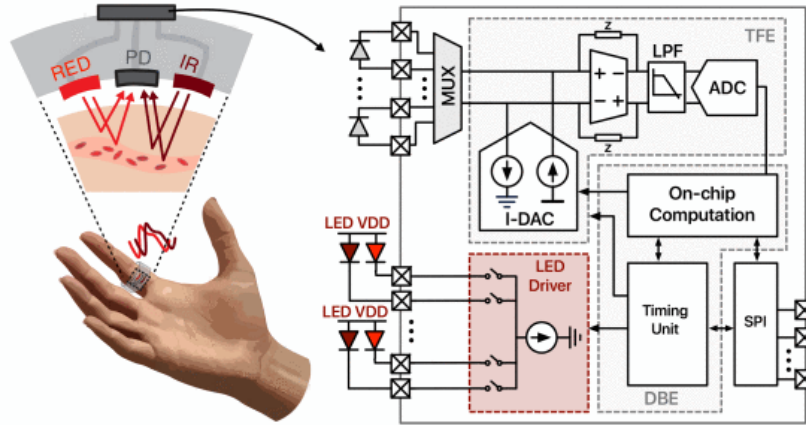


Figure 2.7: Reflectance mode pulse oximetry and typical SpO_2 sensing IC block diagram with the LED drivers, transimpedance frontend (TFE), on-chip digital back-end (DBE), and serial peripheral interface (SPI). Figure from Alamouti (2022). [158]

The proposed sensor IC features an on-chip reconstruction-free sparse sampling algorithm to reduce the overall system power consumption by 70% while maintaining the accuracy of readings. The designed frontend is compatible with a wide range of sensors from silicon PDs to organic PDs with parasitic capacitances up to 10 nF. Implemented in a 40 nm HV CMOS process, the chip occupies 2.43 mm² and consumes 49.7 μW and 15.2 μW of power in continuous and sparse sampling modes, respectively. The performance of the sensor IC was verified in vivo with both types of devices and the results are compared against a clinical

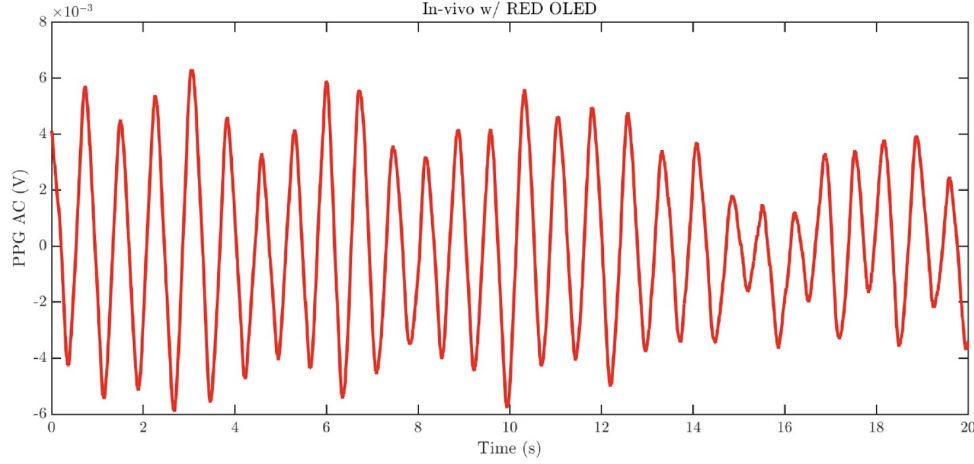


Figure 2.8: Example of a pulse waveform of a participant recorded with using red OLED and commercial photodiode.

grade reference.

An example of the pulse signal collected with a single red OLED is shown in Figure 2.8. The value of SpO_2 is computed based on the ratio of AC component over the DC component of two PPG waveforms. The sparse mode algorithm is shown in Figure 2.9. The sensor begins measurement by uniformly sampling the PPG signal at 100 Hz (continuous mode). The period of the AC component (T) is learned over multiple cycles. Once a stable value is realized, the sensor enters the sparse mode where it predicts the upcoming peaks and valleys (PAVs) and takes a few samples centered around them. A window size (W) of $T/8$ is initially selected and reduced after detection of PAVs. Decreasing W decreases the number of samples taken and consequently decreases the power used. However, a larger observation window will increase accuracy during the presence of high heart rate variability. Thus, Cycle-to-cycle updates are made to the estimated value of T to adjust for any period drift.

Sparse mode may be interrupted by motion artifacts or rapid drifts in heart rate. During this time, if PAVs are repeatedly missed, the sensor expands its observation window by increasing W . If no new PAVs are found within a given W_{max} , the sensor reverts to continuous mode operation. After this transition, the backend re-learns the signal period and the system re-enters sparse mode. This ensures the measurement is not compromised due to duty cycling.

A set of in vivo experiments were performed with the sensor in both continuous and sparse modes of operation. In these experiments, the sensor was placed on the index finger

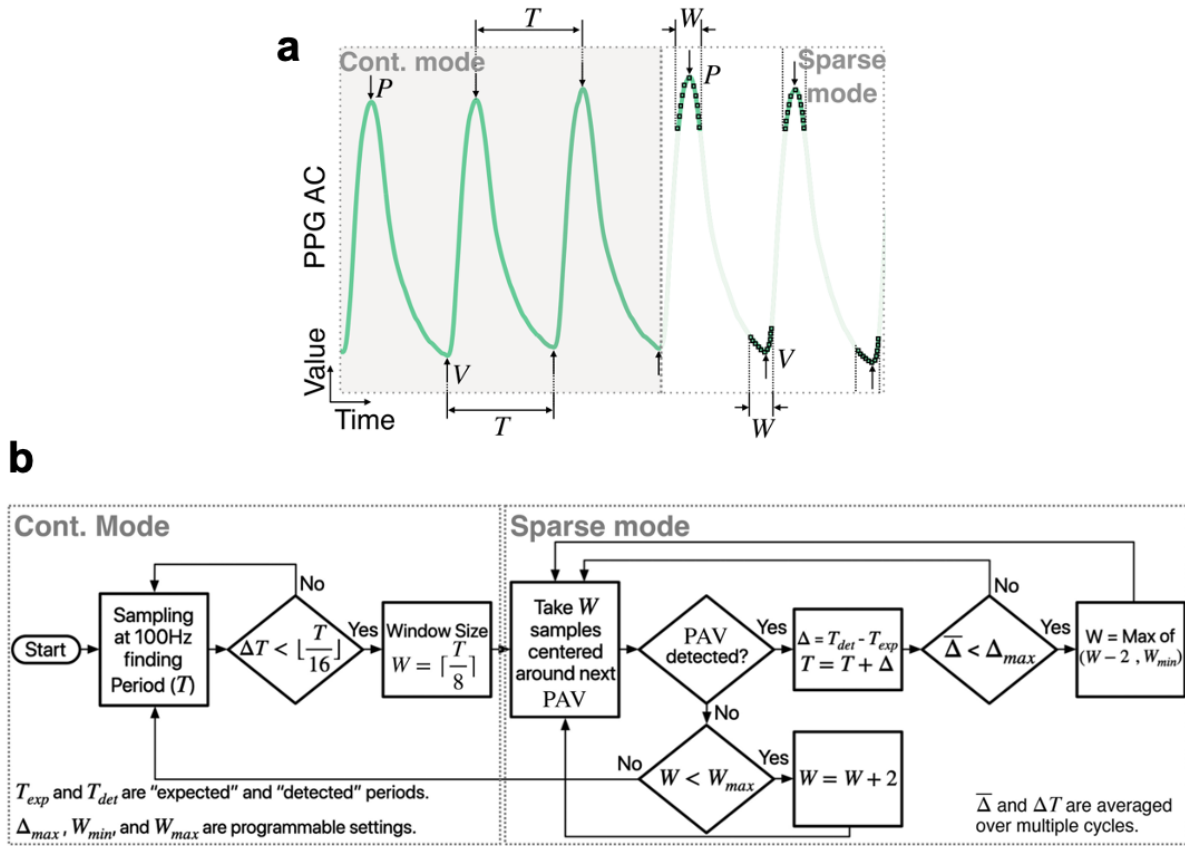


Figure 2.9: a) Graphical illustration of the sparse sampling algorithm described with P and V representing the PPG signal peak and valley signals, T representing the period of the detected PPG signal, and W representing the sparse mode operation window. b) Sparse sampling algorithm flow chart. Figure adapted from Alamouti (2022).[158]

of a healthy participant in a sitting position, under typical incandescent lighting and at room temperature as seen in Figure 2.10. To evaluate the accuracy of the sensor output, a clinical grade pulse-oximeter (Wellue HPO) was attached to the subject's ring finger to perform measurements simultaneously with the sensor IC. First, to verify functionality of the sensor IC's sparse sampling algorithm, commercial PDs and LEDs were used and the PPG signal, the HR, and the SpO_2 results were recorded. Figure 2.11 plots these results against data from the clinical reference. Continuous mode is conducted for 30 seconds then sparse mode is activated. Figure 2.11a-c show an example PPG waveform, SpO_2 , and HR evaluated from a single measurement. The accuracy of the sensor was maintained after transitioning to sparse mode where the HR and SpO_2 mean absolute errors only rose from 0.3 bpm and 0.5% to 0.4 bpm and 0.7% respectively. The errors were computed based on

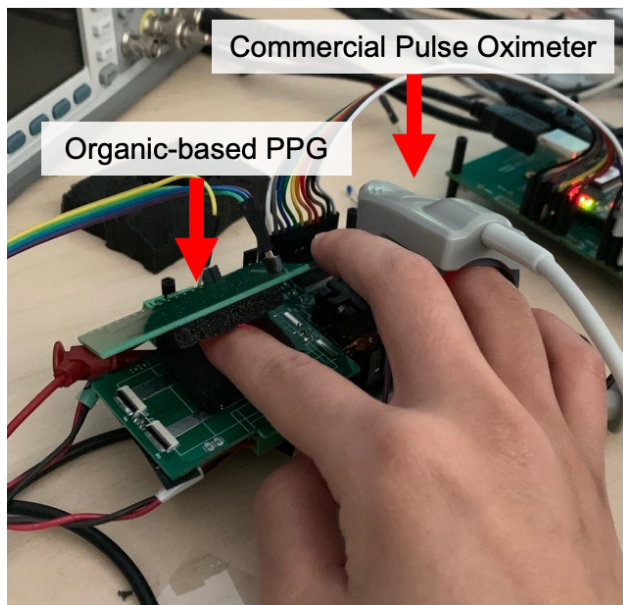


Figure 2.10: Image of test setup with both an organic-based PPG and commercial PPG sensor on the subject's index and ring fingers, respectively. Simultaneous measurements are used to validate the accuracy of the custom IC with organic-based PPG sensors.

the total 40 seconds duration of the recording. Figure 2.11 d and e shows a set of 30 similar recordings of HR and SpO_2 measurements between a HR of 75 to 95 bpm and SpO_2 of 96 to 99%. The measurements taken in sparse mode is plotted against the clinical reference. The measured standard deviation of error for HR and SpO_2 recordings were 0.24 bpm and a 0.21% respectively.

The same measurement was performed using a set of organic devices with a healthy participant. Red and NIR OLEDs were used in this validation as the two colors enable deeper skin penetration. The red and NIR OLEDs exhibited about 5.7 nF and 6.2 nF of parasitic capacitance respectively and required about 5–7 V of forward voltage at 10 mA of current. The OPD had a measured parasitic capacitance of 4.8 nF and less than 10 nA dark current at 0 bias. The PPG waveform, and the corresponding measured HR and SpO_2 are plotted in Figure 2.12 in both continuous and sparse modes. Figure 2.12 a-c show an example PPG waveform, SpO_2 , and HR evaluated from a single measurement. The sensor achieved less than 1 bpm and less than 1% HR and SpO_2 errors when compared against the clinical reference. The use of organic devices required a higher drive voltage (8 V), an increased drive current as well as a higher (0.5%) duty cycle ratio. However, enabling sparse mode significantly lowered the OLED power by about 75%, improving sensor battery life.

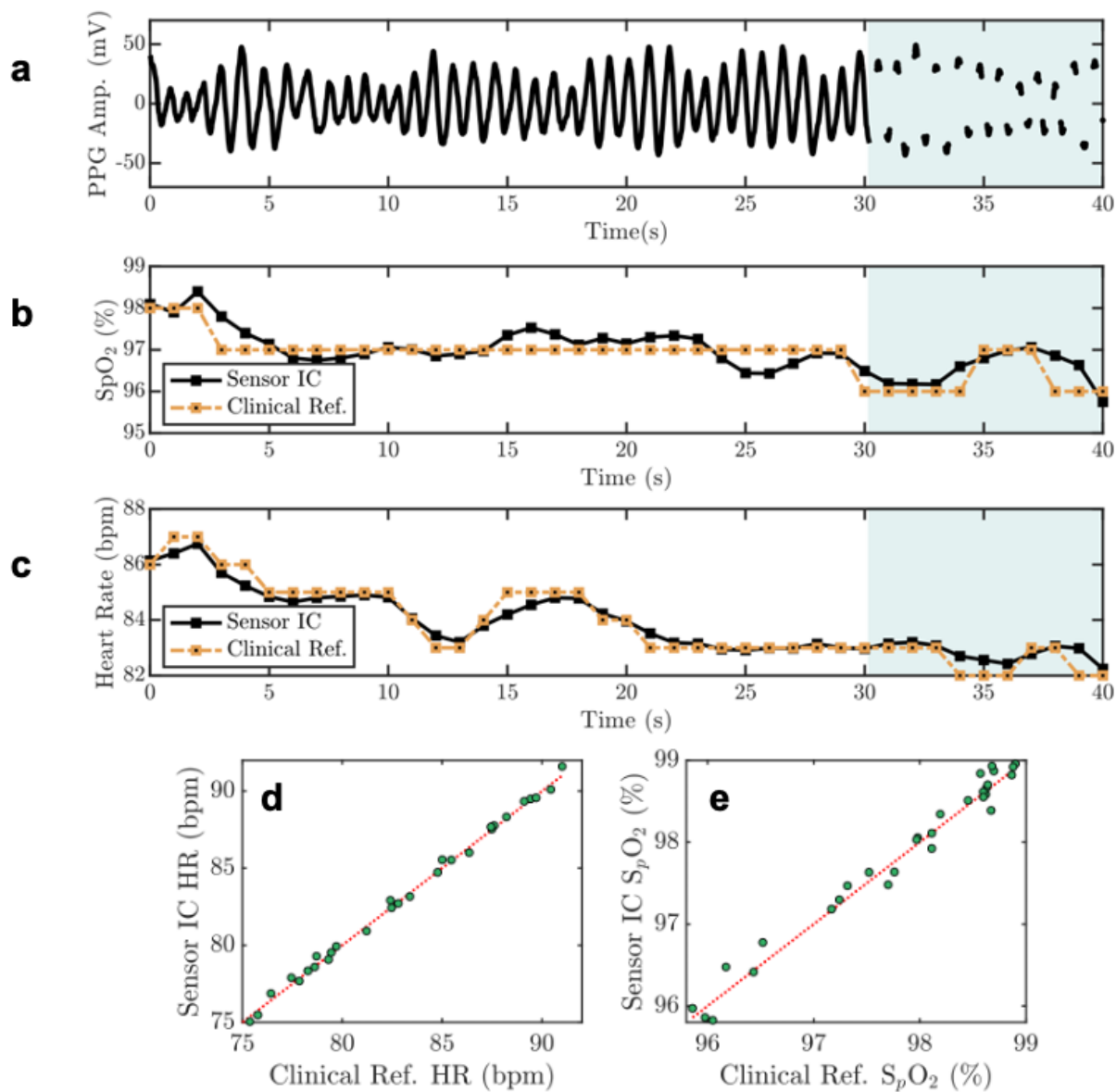


Figure 2.11: In vivo verification of the sensor IC in both continuous and sparse modes using commercial silicon PD and LEDs. a) The PPG waveform and b) its corresponding HR and c) SpO_2 measurements are shown. d) HR and e) SpO_2 measurements from a set of 30 recordings using silicon PD and LEDs. The red dotted line shows the fit line. Figure from Alamouti (2022)[158].

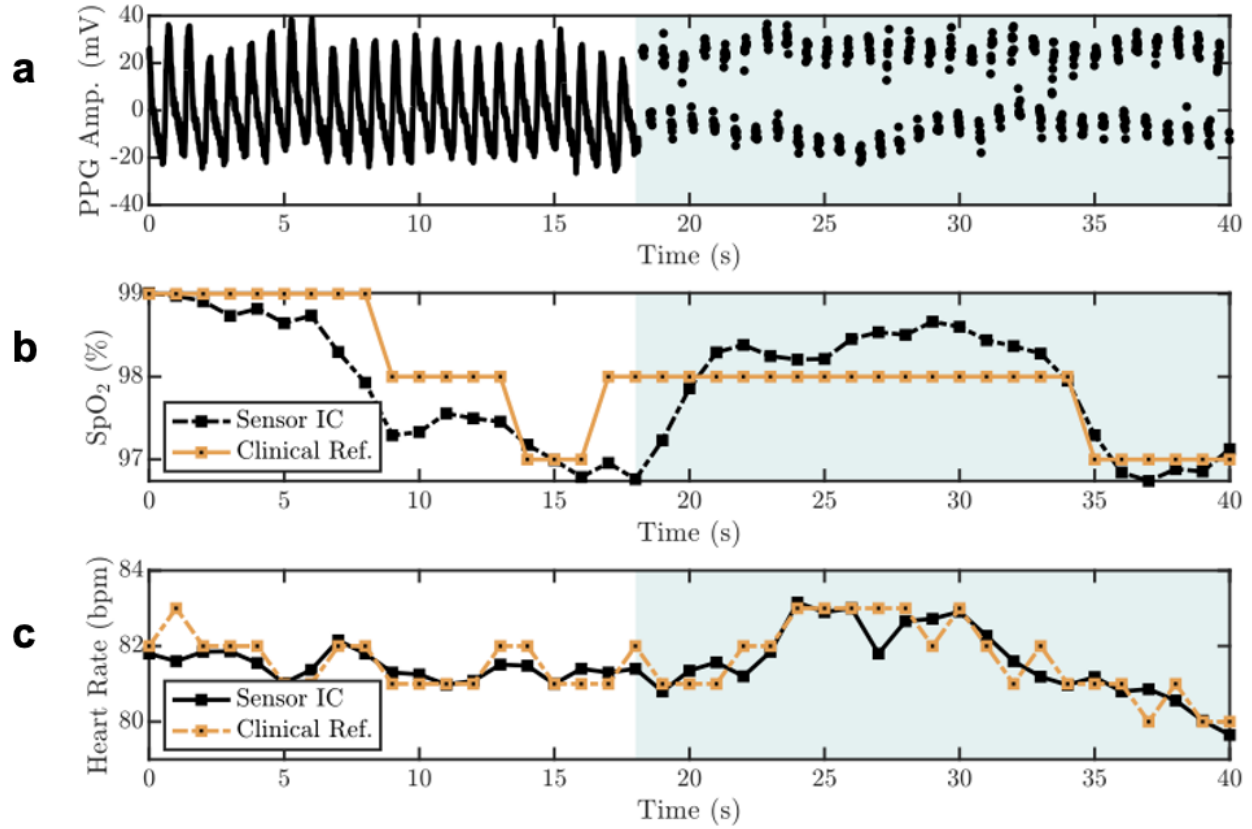


Figure 2.12: In vivo verification of the sensor IC in both continuous and sparse modes using organic-based PPG devices (a red and NIR OLED and a single OPD). a) The PPG waveform and b) the corresponding HR and c) SpO₂ measurements are shown. Figure from Alamouti (2022)[158].

2.6 Conclusion

Overall, the functionality and performance of the proposed sensor IC was characterized using both commercial and organic devices. The in vivo measurement results confirm the accuracy of the sensor data when operating with both inorganic and organic devices. The use of organic devices required a higher drive voltage (8V) and increased drive current as well as a higher (0.5%) duty cycle ratio. This resulted in overall higher power consumption. However, the introduction of reconstruction-free sparse sampling reduces the overall system power by nearly 70% while maintaining the accuracy of the output data. Compared to state-of-the-art, this work achieves the lowest LED power and one of the lowest total power consumption while delivering the lowest input referred noise [153]. Less than 1 bpm and 1% mean absolute errors were achieved in both continuous and sparse modes of operation. With

a sensor IC developed for use with both inorganic and organic devices, this work demonstrates an important step towards low-cost, efficient, and comfortable health monitoring systems.

Chapter 3

Simultaneous Blade-coating of Devices

3.1 Overview

In many flexible electronic applications, integration of multiple devices is necessary. For example, a combination of LEDs and photodiodes are necessary for photoplethysmogram (PPG) and pulse oxygenation measurements [77–84, 153, 158–160]. Fabrication of such a dual device system requires a series of separate time-consuming printing steps optimized for each device. This can be seen in the blade-coated organic reflectance oximeter array in Figure 3.1 where multiple processing steps, materials, and substrates are necessary to complete the optical system [85]. It can be seen that two separate substrates and separate fabrication flows are necessary to realize the optical system. Configuring connections between devices on separate substrates to external circuitry can also add complexity to the integration. Additionally, these applications often require devices to be stacked atop each other. Given that the devices are fabricated on separate flexible substrates, stacking reduces the overall mechanical flexibility of the system. Overall, there is a need to reduce process complexity and fabrication time of multifunctional systems.

Blade coating is a printing method that has been used for fabrication of organic devices including thin-film transistors [107, 108], light-emitting diodes [109–111], photodiodes [49, 112], and photovoltaics [113]. With this method, large-area films can be tuned to the desired film thickness through optimization in coating speed, blade height, processing temperature, and solution properties [161, 162]. Traditionally, a blade coating process is designed for depositing one film at a time, limiting its use to single function systems. We have previously shown a method to blade-coat two light-emitting diodes in a single printing step [109]. To advance this work, we demonstrate the simultaneous deposition of an organic photodiode (OPD) and organic light-emitting diode (OLED) side-by-side on a single flexible substrate. Whereas there may be tolerance for two OLED solutions to intermix during blade coating

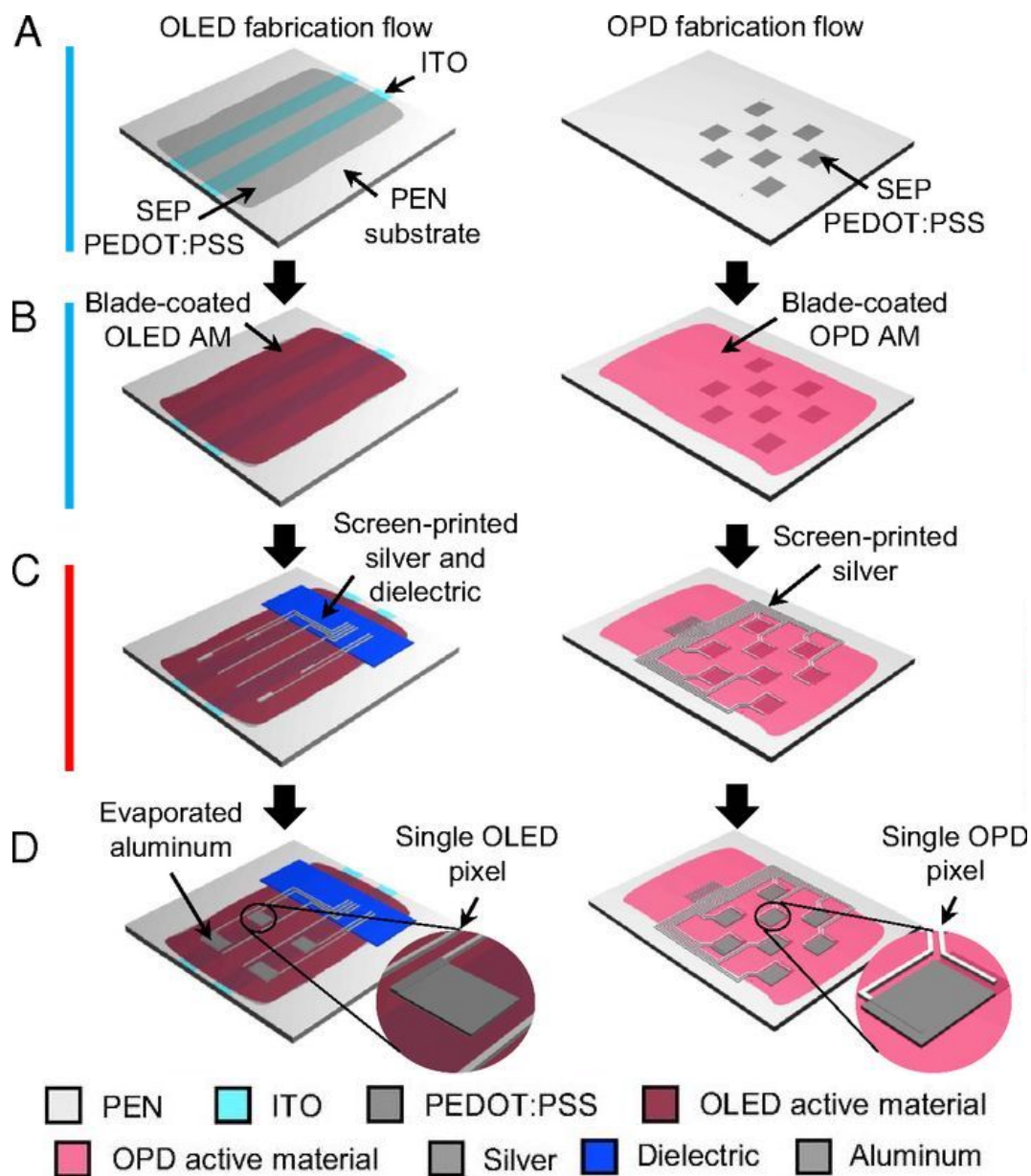


Figure 3.1: The OLED and OPD array fabrication steps are shown side by side. For the OLED array, only one color consisting of 4 pixels is shown for simplicity—the same fabrication steps are used for red and NIR OLEDs. For the OPD array, the complete array consists of 8 pixels. A) PEDOT:PSS is blade coated on ITO-patterned PEN for the OLEDs and on a PEN for the OPDs. B) Active layers are blade coated on top of the PEDOT:PSS. C) Silver traces are screen printed on both OLEDs and OPDs. The OLEDs require an additional dielectric layer (blue) to prevent shorting of the anode to the cathode. D) Calcium/aluminum or aluminum cathode is evaporated for the OLEDs and OPDs, respectively. This defines the active area of each pixel. The insets show a zoomed-in view of the individual pixels. Figure adapted from Khan (2018)[85].

without significantly affecting the final emission of either OLED, OPD and OLED materials are functionally distinct and require more controlled separation of the deposited solutions. The surface of the substrate is treated and patterned to isolate the two solutions during blade coating. Additionally, OPD and OLED devices require different active layer film thicknesses for optimal device performance. We tuned solution concentrations to achieve the desired film thicknesses and optimize device characteristics. Overall, we demonstrate deposition of multifunctional devices on a single substrate. This method accelerates fabrication time, retains flexibility of a single substrate system, and decreases integration complexity for flexible electronic applications.

3.2 Simultaneous Deposition

3.2.1 Defining Print Regions

Definition of print regions is based on the surface energy patterning technique [107, 109, 110]. A self-assembled monolayer (SAM) of hydrophobic fluoroalkylsilane is vapor deposited on a polyethylene naphthalate (PEN) substrate patterned with sputtered indium-tin-oxide (ITO) as the transparent conductive electrodes. Polyimide tape is applied as a protection mask for SAMs in designated regions, and the substrate is exposed to low energy plasma. The result after removing the polyimide tape is a substrate surface with two hydrophilic printing regions surrounded by hydrophobic boundaries. An illustration of this surface energy patterning is shown in Figure 3.2.

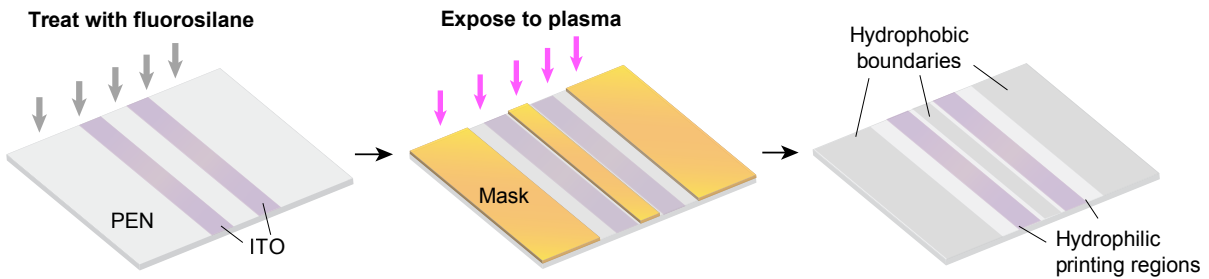


Figure 3.2: Surface energy patterning for simultaneous deposition is illustrated. The ITO/PEN patterned substrate is treated with a blanket vapor deposition of a hydrophobic silane. Polyimide tape is applied in designated regions and the substrate is exposed to plasma, resulting in two hydrophilic printing regions surrounded by hydrophobic boundaries on the surface of the flexible substrate.

With distinct print regions defined on the surface of the substrate, the solutions can now be deposited. This surface energy patterning can be scaled to increase the number of print regions and expand the functionality of the final device system. For instance, this method has been used to fabricate multicolored OLEDs [110].

All blade coating steps were completed on hotplates with a doctor blade and linear actuators. In the case where an OPD and an OLED are deposited side-by-side, the organic layers for both devices are then deposited via blade coating. First, Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is deposited via blade coating. The PEDOT:PSS is applied to the top of the print region, or the "solution reservoir". A single doctor blade is used to print the two PEDOT:PSS films on the print regions at a blade height, coating speed, and hotplate temperature of $50\text{ }\mu\text{m}$, 1.8 cm s^{-1} , and 90°C , respectively. An illustration of the printing steps are shown in Figure 3.3.

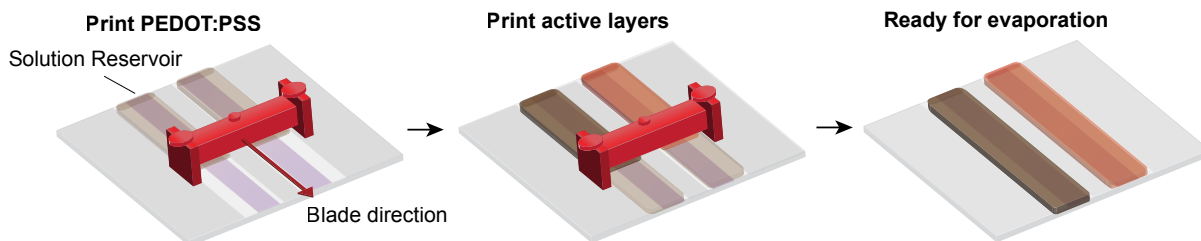


Figure 3.3: Simultaneous deposition of OLED and OPD films. PEDOT:PSS and active layers of the organic optoelectronic device stacks are all printed via blade coating.

Next, the active layers are printed. Similarly, the individual solutions are applied to the solution reservoir for the respective device: the bulk heterojunction (BHJ) for the OPD and electron blocking layer (EBL) and later the emissive layer (EML) for the OLED. Semiconducting organic materials used for OPD BHJ, OLED EBL, and EML were provided by Cambridge Display Technologies (CDT). The OLED electron blocking and emissive materials provided were dissolved in *o*-Xylene. The electron blocking interlayer is printed for the OLED stack at a blade height, blade speed, and hotplate temperature of $50\text{ }\mu\text{m}$, 1.8 cm s^{-1} , and 65°C followed by annealing at 180°C for 1 hr. After annealing, the hotplate is cooled and reset to 65°C for printing the OPD BHJ and OLED EML at a blade height and speed of $200\text{ }\mu\text{m}$, 1.8 cm s^{-1} . The films were annealed at 140°C for 30 min.

Finally, top electrodes are then thermally evaporated onto the printed organic layers to complete the device stack. For OPDs, this is a 80-100 nm thick layer of aluminum.

For OLEDs, this is a 5-10 nm thick layer of calcium, followed by a 80-100 nm thick layer of aluminum. The OLEDs are also encapsulated with a UV curable epoxy and plastic coverslip. Figure 3.5 shows an image of dried films after printing steps are completed and Figure 3.4 shows schematic of the full device stacks fabricated in this work [163].

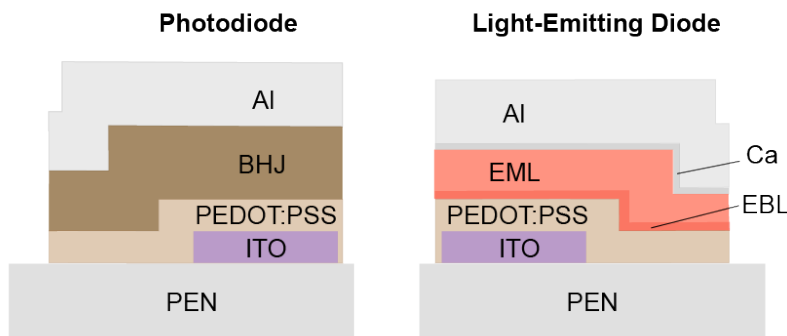


Figure 3.4: Illustration of complete film stacks for the simultaneously blade-coated OPD and OLED. Both OPD and OLED employ a conventional device architecture with ITO, PEDOT:PSS and active material. The OLED also utilizes an electron blocking layer and calcium cathode for improved charge transport characteristics.

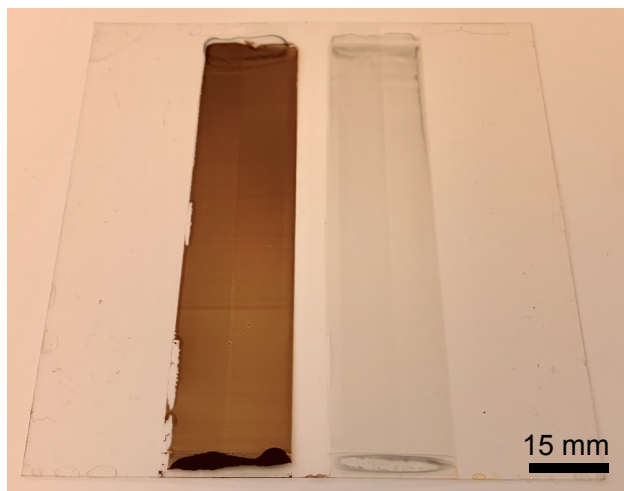


Figure 3.5: Image of dried films after printing and prior to evaporation. The simultaneously blade-coated OPD (left) and OLED (right) are deposited on a transparent flexible PEN substrate. The PEN shown here is roughly 10 cm x 10 cm in area.

3.2.2 Solution Intermixing

As previously discussed, OPD and OLED materials are functionally distinct. Isolation of the OPD and OLED solutions is crucial as inadvertent contact between the two semiconducting materials results in a loss of device functionalities. OPD BHJ materials are optimized for efficient absorption of photons and dissociation of excitons in response to light whereas OLED EML materials are optimized for generation and recombination of excitons in response to injected current. These opposing optoelectronic mechanisms interfere when the two materials are mixed, negatively affecting device performances. This can be seen in Figure 3.6.



Figure 3.6: Illustration and images of merging effect on simultaneous printing. In this scenario, the OPD BHJ solution travels across the blade to the OLED side. Mixing with the OLED EML solution, the OPD BHJ solution leaves a streak of photoabsorbing along the edge of the OLED film, impacting the emissive area of the OLED. Dim emission of an OLED pixel is shown as a result as the OPD intermixing. The emission area is both smaller than intended and nonuniform.

During printing, separation of solutions along both the substrate and the blade are necessary as the materials are still wet and have the mobility to coalesce. Water contact angles are typically used to assess the wettability of a liquid on a surface. This is useful if the solution to be deposited is water based, such as PEDOT:PSS. However, this may not always be the case. In this work, organic layers are subsequently deposited on top of various layers in the device stack. For instance, the bulk heterojunction (BHJ) of the OPD is printed atop the dried PEDOT:PSS layer. Thus, the contact angle of a BHJ droplet on the PEDOT:PSS surface will indicate the wettability and better represent the BHJ deposition.

Contact angle measurements were used to analyze the wettability of various solutions on each surface in this process. Figure 2 shows contact angles of water (a-c), OLED EML solution (d-f), and OPD BHJ solution (g-i) on the surfaces of the fluorosilane (green), the printing region (orange), and the doctor blade (blue). Water spreads on the surface of the printing region (contact angle $< 5^\circ$) and dewets on the hydrophobic fluorosilane (110°). Furthermore, water is hydrophobic on the surface of the doctor blade, exhibiting incomplete

wetting with a contact angle of 90° . As a result of the high contrast in wetting behavior between the printing region and the other two surfaces, no merging of PEDOT:PSS, a water-based solution, was observed. On the other hand, the contact angle disparity for the organic solutions is smaller. On the printing regions, organic solutions exhibit complete wetting ($< 5^\circ$) and partial wetting (45° and 50°) on the print area and fluorosilane, respectively. However, organic solutions achieve good wetting (35° and 30°) on the blade surface. Thus, the organic solutions were observed to spread along the blade and coalesce during printing when there is an excess of solution. This can be seen in Figure S1 where the OPD BHJ solution merged with the OLED EML solution via travel across the blade. To mitigate this issue, deposited solution volume was optimized to decrease spreading and avoid solution merging.

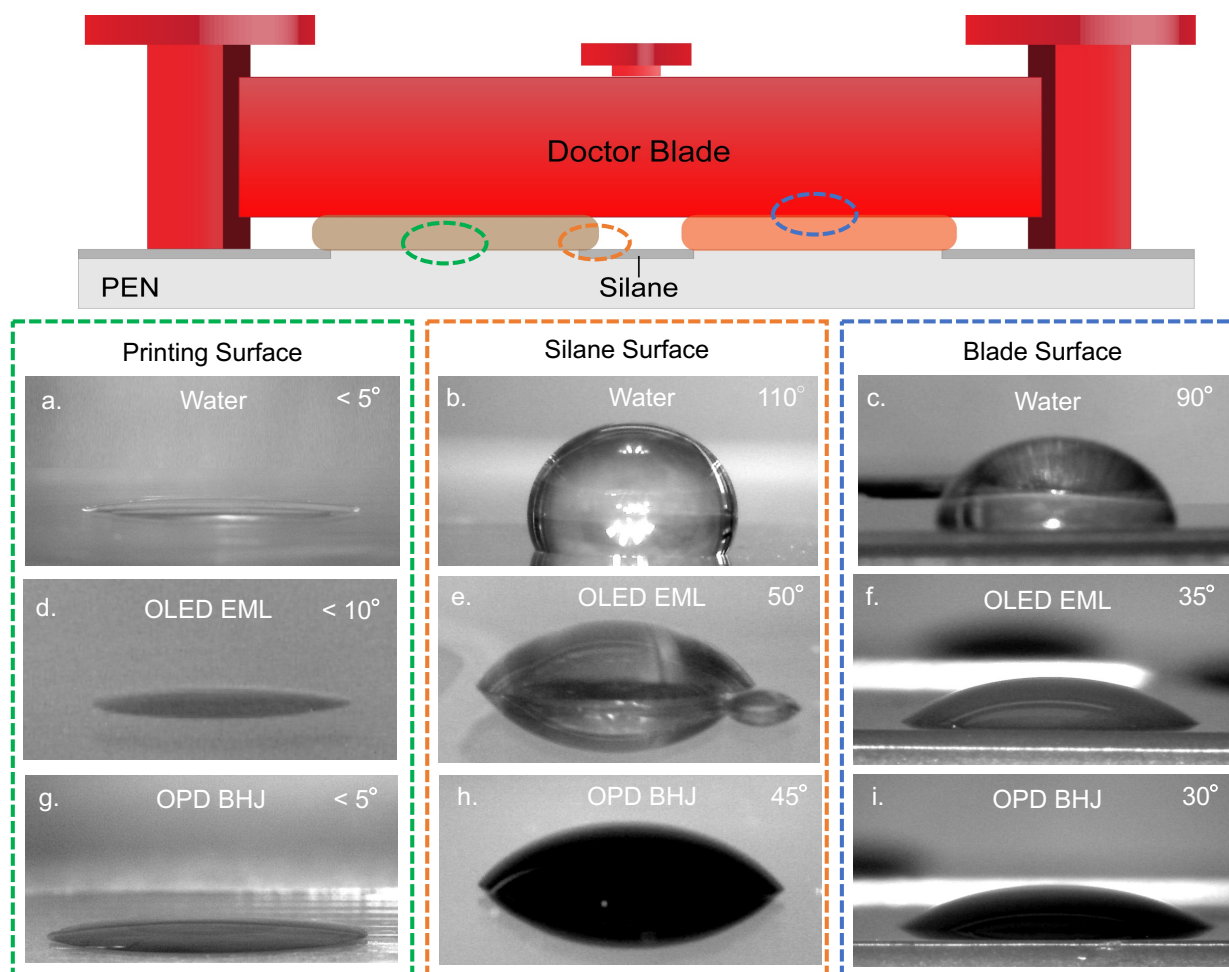


Figure 3.7: The contact angles of solutions on three surfaces used in this process. The three solutions are water, the OLED EML solution and the OPD BHJ solution. (a, d, g in green) The solution – print area interface shows complete wetting for all three solutions. (b, e, h in orange) The solution – fluorosilane interface shows water has the highest contact angle with OLED and OPD showing similar partial wetting behavior on the surface of fluorosilane. (c, f, i in blue) The solution – blade interface shows that water spreads the least on blade surface, while both organic solutions exhibit good wetting on the blade surface.

3.3 Material and Process Optimization

3.3.1 Solution Concentrations and Viscosity

Organic materials are optimized to achieve high device performance [36, 164]. Based on desired device characteristics, the blade coating parameters are optimized for the thickness of the resulting film. The printed film thickness t is related to blade coating parameters in equation 3.1 where $t_{wetfilm}$ is the wet film thickness, μ is the solution viscosity, V_{blade} is the blade velocity, γ is the solution surface tension and $R_{meniscus}$ is the radius of curvature of the solution trailing the moving blade [161].

$$t_{wetfilm} \propto \left(\frac{\mu V_{blade}}{\gamma} \right)^{2/3} R_{meniscus} \quad (3.1)$$

Contrary to spin coating where film thickness is inversely related to the spin rate, blade-coated film thickness is directly proportional to the coating speed. A decrease in coating speed results in a decreased film thickness. Similarly, a decrease in solution concentration results in a decrease in solution viscosity and thus a decrease in film thickness.

OPD BHJ solutions were prepared at various concentrations and measured with a Brookfield Model DV-III Programmable Rheometer attached with a CP-40 cone spindle. The viscosity of various OPD BHJ solutions are shown in Figure 3.8

Both these parameters enable tunability of device performance through optimization of the film thickness. This is shown in Figure 3.9 where the average EQE performance of OPD devices were tuned with adjustments in both coating speed and solution concentration. Devices fabricated from 50 mg mL⁻¹ BHJ solution and coating speed of 2.0 cm s⁻¹ (green) shows roughly 30% EQE at a measured film thickness of 165 nm. Decreasing coating speed from 2.0 cm s⁻¹ to 1.8 cm s⁻¹ decreased the film thickness to 140 nm, resulting in improved peak EQE to 44% at 800 nm (orange). Using the same coating speed of 1.8 cm s⁻¹ with decreased the BHJ solution of 40 mg mL⁻¹, the film thickness decreased to 110 nm and further improved the peak EQE to 53% at 800 nm (blue).

Traditionally in blade coating, one solution is deposited for each printing layer and processing parameters are optimized for that single film. In this work, OPD and OLED solutions are simultaneously printed side-by-side in a single blade coating step. Thus, the blade height and speed, substrate temperature, and annealing conditions are shared processing conditions for both solutions. However, OPD and OLED active layers can require different target film thicknesses to optimize desired device characteristics. OPD BHJ and OLED EML solutions can also have distinct viscosity and wetting properties, adding complexity to

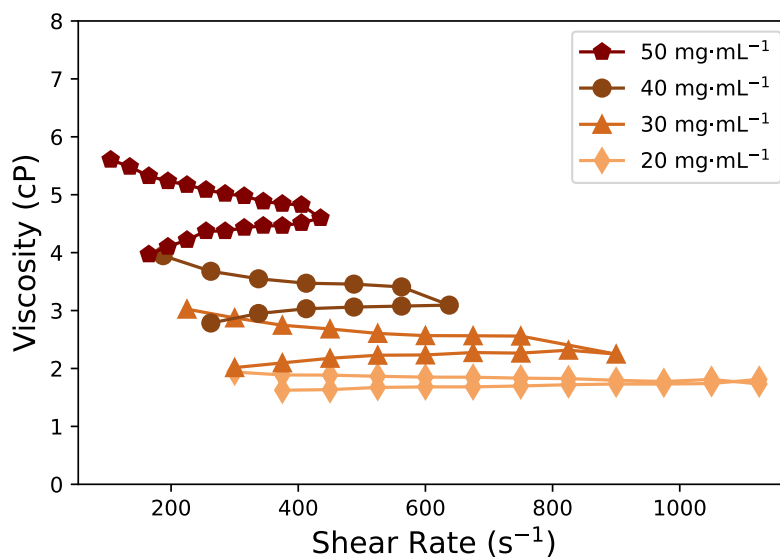


Figure 3.8: Viscosity versus shear rate of OPD BHJ solution at concentrations of 50, 40, 30, and 20 mg mL^{-1} .

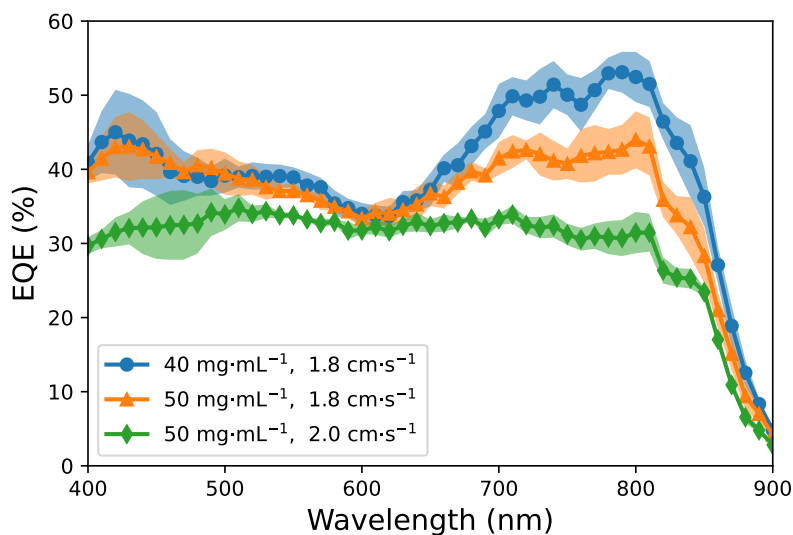


Figure 3.9: EQE performance of OPDs printed with a combination of coating speeds of 2.0 cm s^{-1} and 1.8 cm s^{-1} and BHJ solution concentrations of 50 mg mL^{-1} and 40 mg mL^{-1} . All other processing conditions were kept constant. The resulting film thicknesses were 165 nm (green), 140 nm (orange), and 110 nm (blue). EQE was measured at zero applied bias.

developing a single process for dual-device prints. An advantage of SEP is the isolation of two solutions, allowing individual films to be tuned via solution rheological properties such as solution concentration as previously shown. Furthermore, adjusting individual solution concentrations rather than blade speed enables tuning of one film without affecting the other.

Here, the fabrication process is optimized by chosen figure of merits for each device – spectral responsivity $R(\lambda)$ for OPDs and luminance L_v for OLEDs. The spectral responsivity of a photodiode determines the application space of a photodetector as it quantifies the electrical output of a detector in response to optical input over a range of wavelengths. $R(\lambda)$, in units of A W^{-1} , is defined as the ratio between photocurrent generated I_L and incident optical power P_L as a function of wavelength. The equation is given below where η is the external quantum efficiency of the detector for a given wavelength, q is the elementary charge, f is the frequency of the incident light, h is Planck's constant, and c is the speed of light.

$$R(\lambda) = \frac{I_L}{P_L} = \frac{\eta q}{hf} = \frac{\eta q \lambda}{hc} \quad (3.2)$$

Luminance L_v , in units of $\text{cd} \cdot \text{m}^{-2}$, is a photometric measure of radiance $L(\lambda)$ and is a critical parameter for lighting and display applications. The equation for luminance is given by below where $V(\lambda)$ is the visual response of the human eye, I_{det} is the measured photocurrent at the detector, D is the distance between the OLED and the detector, $R_{\text{det},s}$ is the detector responsivity weighted to the measured OLED emission spectrum, S_0 is the OLED emission area, and A_0 is the detector area.

$$L_v = 683[\text{lm/W}] \int_{380}^{770} L(\lambda) \cdot V(\lambda) d\lambda = 683 \int_{380}^{770} \frac{I_{\text{det}} D^2}{R_{\text{det},s} S_0 A_0} \cdot V(\lambda) d\lambda \quad (3.3)$$

Figure of merits were characterized for devices fabricated from various solution concentrations. The film thicknesses were conducted by printing corresponding OPD BHJ and OLED EML films on plasma treated glass substrates and measuring the thickness with a Keyence VK-X1000 Laser Scanning Confocal Microscope. As the thicknesses of thin organic films stacked atop a flexible substrate can be difficult to measure, film thicknesses were measured from OPD BHJ and OLED EML films printed on plasma-treated glass for simplification. The wettability of organic solutions on plasma-treated glass and on the corresponding printing surface, discussed previously in Figure 3.7, have negligible differences 3.10. Thus, the films measured on glass are expected to provide film thicknesses suitable for

correlating characteristics for devices fabricated from different solution concentrations.

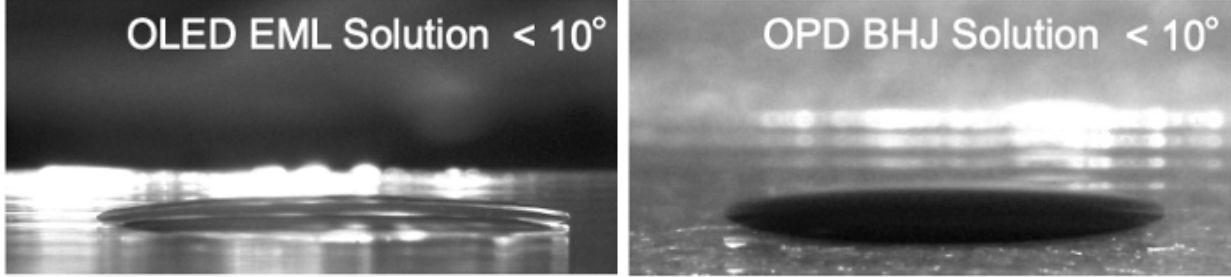


Figure 3.10: Contact angle images of OLED EML solution and OPD BHJ solution on the plasma treated glass. Both exhibit good wetting with a contact under under 10 degrees.

For OPDs, BHJ solution concentrations of 40, 30, and 20 mg mL⁻¹ were used resulting in film thicknesses of 110, 75, and 42 nm. For OLEDs, EML solution concentrations of 12, 10, and 8 mg mL⁻¹ were used resulting in film thicknesses of 70, 55, and 45 nm.

Figure 3.11 shows viscosity versus shear rate for OPD BHJ solutions and the average performance of OPDs printed with the respective solution concentrations. Viscosities ranged from 1.6 to 3.9 cP for OPD BHJ solutions. Each performance curve represents average and standard deviation characteristics measured from 5-10 devices from a single print. The spectral response of OPDs under no applied bias was measured over a broad wavelength range of 400 to 900 nm. Responsivity values at various wavelengths are summarized in Table 3.1.

Table 3.1: Comparison of responsivities at wavelengths of 500, 600, 700 and 800 nm for printed OPDs with BHJ solution concentrations of 40 mg mL⁻¹, 30 mg mL⁻¹, and 20 mg mL⁻¹.

$R[A \cdot W^{-1}]$	$\lambda = 500 \text{ nm}$	$\lambda = 600 \text{ nm}$	$\lambda = 700 \text{ nm}$	$\lambda = 800 \text{ nm}$
40 mg mL ⁻¹	0.15	0.14	0.25	0.33
30 mg mL ⁻¹	0.12	0.097	0.092	0.11
20 mg mL ⁻¹	0.032	0.019	0.013	0.018

The highest overall spectral response was measured from OPDs printed with the 40 mg mL⁻¹ BHJ solution with a peak value of 0.33 A W⁻¹ at 800 nm. Decreasing BHJ solution concentration to 30 mg mL⁻¹ and 20 mg mL⁻¹, the responsivity at 800 nm drops to 0.11

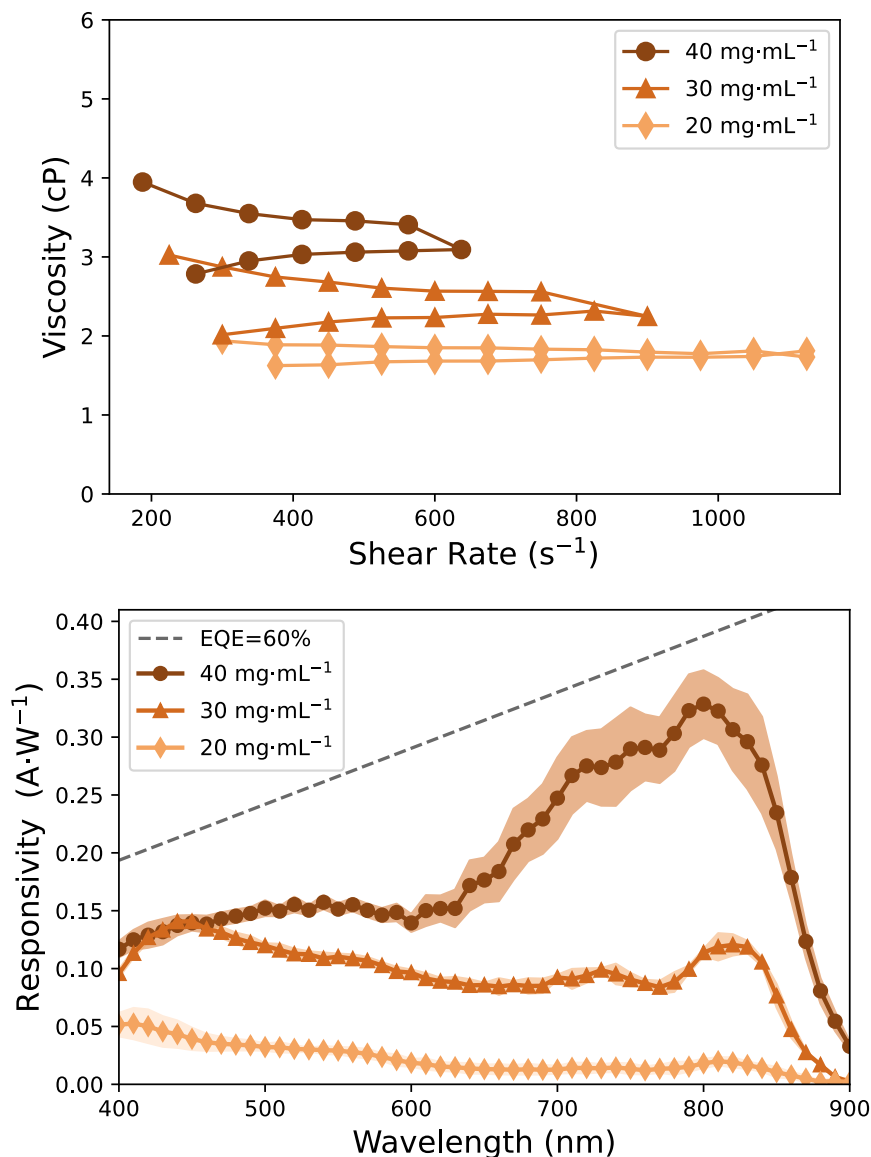


Figure 3.11: Viscosity versus shear rate of OPD BHJ solutions at concentrations of 40 mg mL^{-1} , 30 mg mL^{-1} , and 20 mg mL^{-1} (top). Responsivity of printed OPDs with zero applied bias. Spectral responsivity at an EQE of 60% is plotted as a dashed line for reference (bottom).

and 0.02 A W^{-1} , respectively. OPDs printed with BHJ solution concentrations lower than 40 mg mL^{-1} exhibit poor absorption, shown in Figure 3.12, leading to poor efficiencies. This suggests the ideal BHJ solution concentration for the printing process and material used is around 40 mg mL^{-1} .

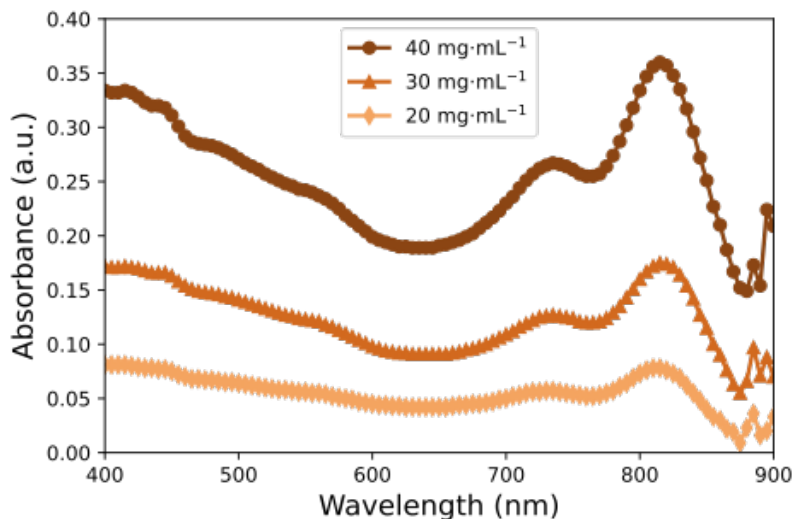


Figure 3.12: Absorbance spectra of OPDs printed with BHJ solutions at concentrations of 40, 30, and 20 mg mL^{-1} .

Figure 3.13 shows viscosity versus shear rate for OLED EML solutions and the average performance of OLEDs printed with the respective solution concentrations. Viscosities ranged from 1.2 cP to 2.7 cP for OLED EML solutions. Similar to the OPD characteristics, each performance curve represents average and standard deviation characteristics measured from 5-10 devices from a single print. Luminance versus voltage performance for three printed OLEDs are shown. Devices from all three solution concentrations exhibit clean diode behavior and average luminance greater than 5000 cd m^{-2} . The electroluminescence spectra measured from OLEDs printed with the three solution concentrations exhibit no noticeable shifts, with consistent peaks at 612 nm, shown in Figure 3.14.

The highest OLED luminance achieved among the three EML solution concentrations was around 7000 cd m^{-2} from 10 mg mL^{-1} , followed by 12 mg mL^{-1} and 8 mg mL^{-1} . Furthermore, the lowest turn-on voltage and lowest operating voltage (voltage required to achieve a luminance of 1000 cd m^{-2}) was achieved with 10 mg mL^{-1} EML solution. The thinnest EML film from the 8 mg mL^{-1} solution had the highest turn-on voltage as well as the largest variability in luminance values. This is attributed to more pronounced exciton quenching for thinner emissive films in which recombination occurs closer to the electrode. Overall, the highest luminance and lowest turn-on voltage was achieved with 10 mg mL^{-1} , summarized in Table 3.2.

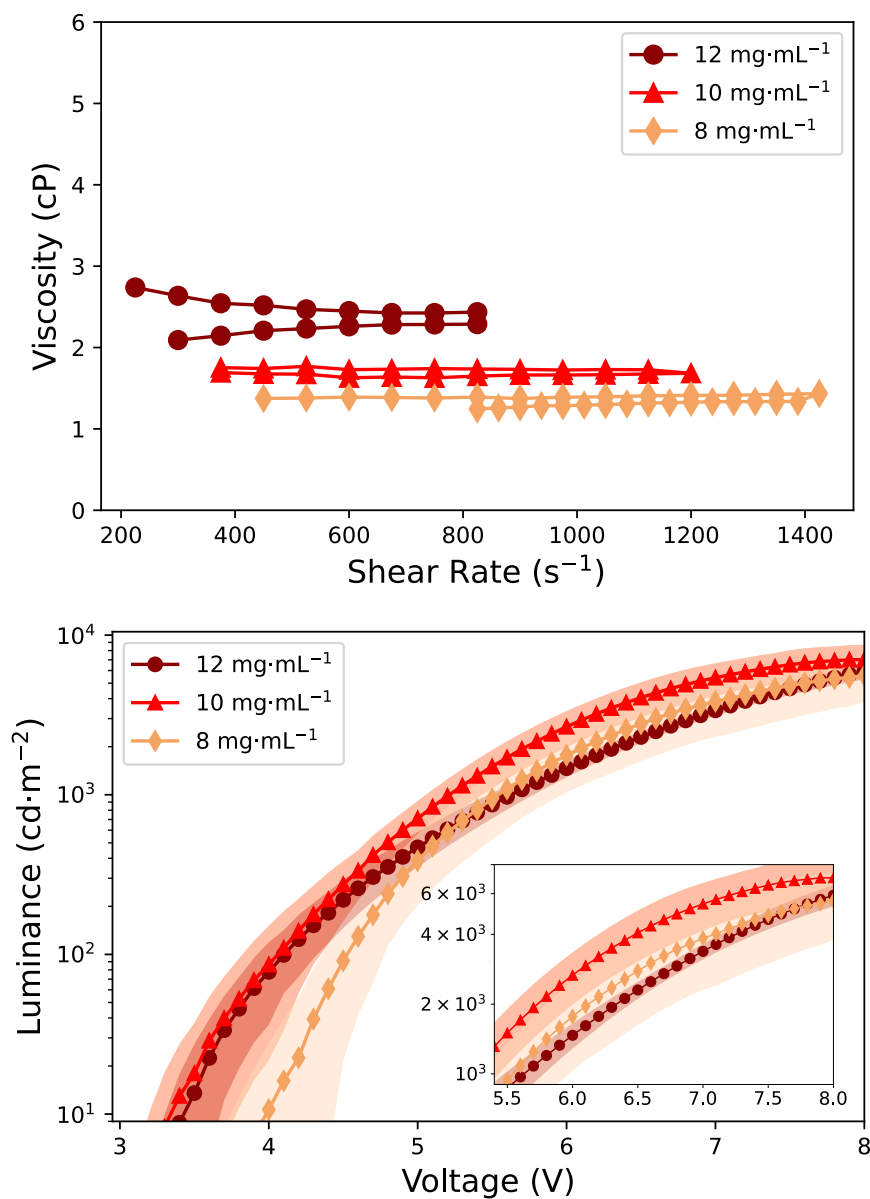


Figure 3.13: Viscosity versus shear rate of OLED EML solutions at concentrations of 12 mg mL^{-1} , 10 mg mL^{-1} , and 8 mg mL^{-1} (top). Luminance of printed OLEDs from 3 to 8V. The inset plot shows detailed luminance behavior between 5.5 V and 8 V (bottom).

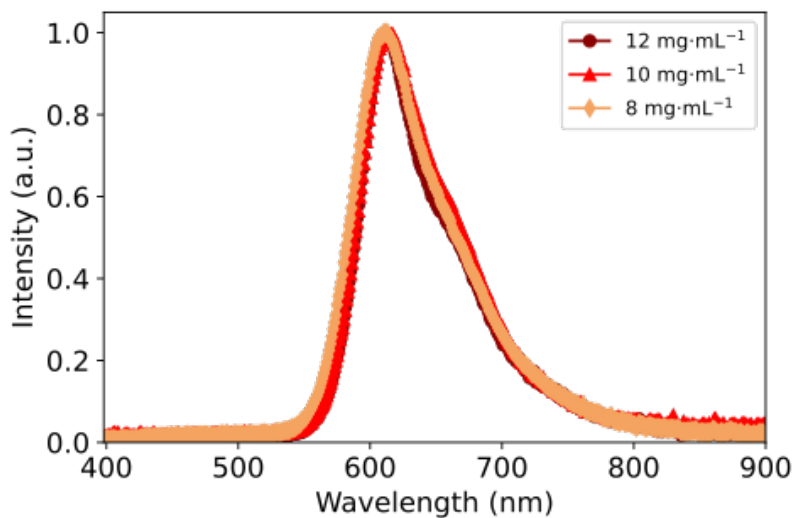


Figure 3.14: Electroluminescence spectra of OLEDs printed with EML solutions at concentrations of 12, 10, and 8 mg mL⁻¹. All spectra exhibit peaks at 612 nm.

Table 3.2: Comparison of turn-on voltage, 1000 cd m⁻² operating voltage, and luminance at 8 V of printed OLEDs with EML solution concentrations of 12 mg mL⁻¹, 10 mg mL⁻¹, and 8 mg mL⁻¹.

	$V_{\text{turn-on}}$ [V]	$V_{L=1000 \text{ cd} \cdot \text{m}^{-2}}$ [V]	$L_{@8V}$ [cd · m ⁻²]
12 mg mL ⁻¹	3.5	5.7	5900
10 mg mL ⁻¹	3.4	5.3	7000
8 mg mL ⁻¹	4	5.6	5600

3.4 Device Characteristics

3.4.1 Printed Organic Photodiodes

Figure 3.15 shows device characteristics of an OPD printed using the optimized BHJ solution concentration of 40 mg mL^{-1} . Current density – voltage (J-V), external quantum efficiency (EQE), linear dynamic range (LDR), and frequency response of a printed OPD is shown. Figure 3.15a shows the semilog plot of J-V characteristics. Photodetectors operate under reverse bias, or photoconductive mode, in which low dark current is desired for detection of low intensity signals. A low dark current of 22 nA cm^{-2} at a bias of -1 V is observed. Under $7 \mu\text{W cm}^{-2}$ illumination at 532 nm , the current density reaches $1.5 \mu\text{A cm}^{-2}$ at -1 V . OPD EQE between 30-40% is observed across the visible spectrum and increases to 40-50% in the NIR spectrum. The EQE profile peaks at 750 nm and 800 nm with efficiencies of 54% and 56%, respectively. The range of intensities in which the detector's electrical response is linear to incident illumination, linear dynamic range (LDR), is expressed by:

$$LDR = 20 \log \frac{i_{\text{lin,max}}}{i_{\text{lin,min}}} \quad (3.4)$$

where $i_{\text{lin,max}}$ and $i_{\text{lin,min}}$ are the maximum and minimum photocurrent in the linear response region of the photodetector. Printed OPDs show good linear response of 88 dB in Figure 3.15c, demonstrating that the device can operate under illumination intensities ranging over four orders of magnitude. Frequency response measures the detection speed of OPDs. The 3 dB bandwidth, or cut-off frequency $f_{3 \text{ dB}}$, is defined as the frequency at which output power of the detector is attenuated by 50% in response to modulating light signals. The equation is given by:

$$-3 \text{ dB} = 20 \log \frac{i(f_{3 \text{ dB}})}{i_0} \quad (3.5)$$

where $i(f_{3 \text{ dB}})$ and i_0 are the photocurrents in response to illumination at the cut-off frequency and steady-state, respectively. The measured cutoff frequency was 300 kHz , as shown in Figure 3.15d.

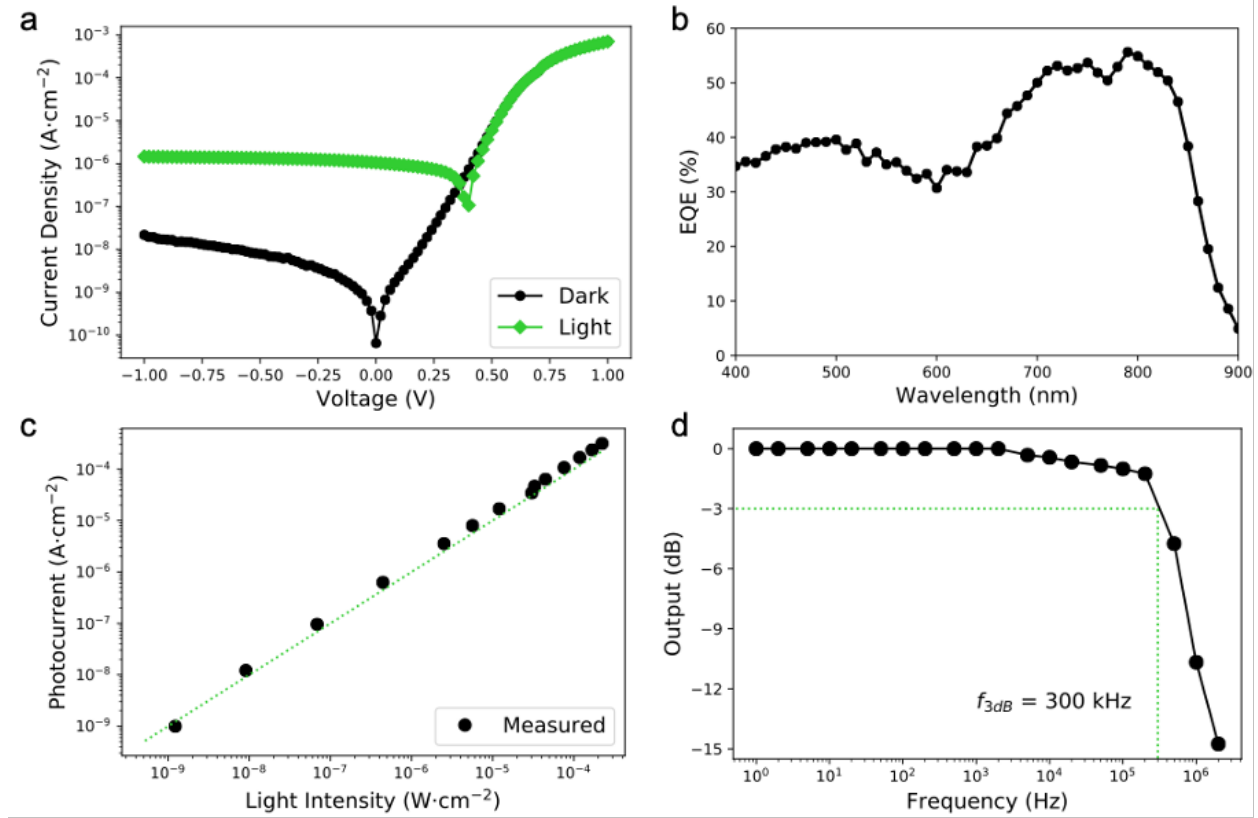


Figure 3.15: Device characteristics of an OPD simultaneously printed using a 40 mg mL⁻¹ BHJ solution concentration. (a) Current density versus voltage (J-V) measured under dark and illumination, (b) external quantum efficiency (EQE) in the wavelength range 400 to 900 nm, (c) linear dynamic range (LDR), and (d) frequency response. Light current, LDR, and frequency response were measured with a 532 nm LED at 7 $\mu\text{W cm}^{-2}$ illumination. No bias was applied to the OPD during EQE, LDR, and cut-off frequency measurements.

3.4.2 Printed Organic LEDs

Figure 3.16 shows device characteristics of an OLED simultaneously printed using the optimal EML solution concentration of 10 mg mL⁻¹. The current density–voltage (J-V), luminance, EQE, luminous efficacy, and electroluminescence spectrum are shown. The OLED exhibits clean diode behavior with a turn-on voltage of 3.1 V at a current density of 1.9 mA cm⁻². A luminance of 7980 cd m⁻² is measured at 8 V. A luminance of 1000 cd m⁻² can be achieved at an operating voltage of 4.8 V. Luminous efficacy η_{lum} is defined as the ratio of luminous flux Φ_v , in lumens, emitted to the electrical input power P , in Watts. It can be expressed as:

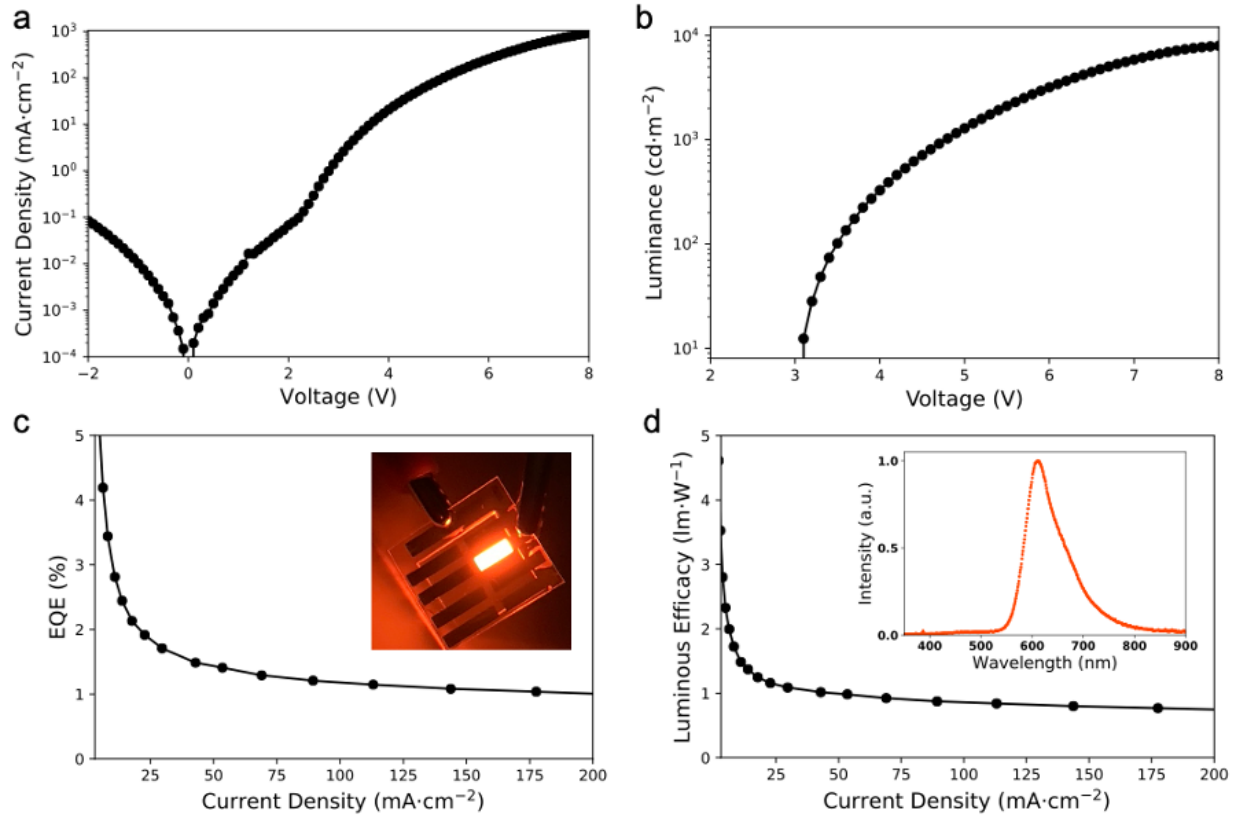


Figure 3.16: Device characteristics of an OLED simultaneously printed using a 10 mg mL^{-1} EML solution concentration. (a) Current density versus voltage (J-V), (b) luminance versus voltage (L-V), (c) EQE versus current density with inset image of OLED operated at 6V, and (d) luminous efficacy versus current density with inset plot of the OLED electroluminescence spectrum.

$$\eta_{\text{lum}} = \frac{\Phi_v}{P} \quad (3.6)$$

Printed OLED EQE and luminous efficacy steadies to roughly 1% and 1 lm W^{-1} , respectively, for current densities above 100 mA cm^{-2} . At a luminance of 1000 cd m^{-2} the EQE and luminous efficacy is 1.2% and 0.9 lm W^{-1} . The inset of Figure 3.16c shows an image of the printed OLED operated at 6 V. The inset of Figure 3.16d shows the electroluminescence spectra of the printed OLED with a peak at 612 nm.

3.5 Conclusion

A method for simultaneous blade coating of two different films is demonstrated. SEP isolates printing regions, enabling the deposition of two functionally opposing materials side-by-side on a single flexible substrate. Here, the OPD BHJ and OLED EML film thicknesses were tuned via adjustments in solution concentrations. This enables the use of a single process for the fabrication of two devices without compromising device performances. The resulting dual device structure eliminates the need for laminating OPD and OLED substrates, retaining the mechanical flexibility of lightweight optoelectronic systems while allowing for simplified integration to electronic circuitry. This method demonstrates an important step towards roll-to-roll printing where integration of devices with different functionalities is needed.

Chapter 4

Organic Solvent Selection Methodology

Solution-processable electronic materials have become increasingly popular due to the potential for roll-to-roll manufacturing, making them highly desirable for low-cost large-scale production [12–14, 165, 166]. These materials span a variety of chemistries such as semiconductor small molecules, polymers, metal nanoparticles, colloidal quantum dots, and hybrid perovskites. With these innovative materials, lightweight, flexible and large-area devices have been demonstrated in a variety of electronic applications including light-emitting diodes, photovoltaics, batteries, transistors, and environmental sensors[103, 112, 119, 163, 167–171].

While record performance for solution processed electronic devices set important benchmarks for new material systems and device architectures, these devices are typically fabricated from low-throughput processing techniques with limited solution quantities. This overlooks the importance of material and solvent considerations at the manufacturing scale. To achieve the promise of high-throughput, roll-to-roll manufacturing, it is important to consider the environmental impacts of the solvent used in the system, especially when the solvent constitutes the majority of the material deposited. Solvent choice for a material system depends on a variety of factors including device architecture, solvent properties, and the desired film characteristics. Typically, the high performing solution processable electronics demonstrated are fabricated without considerations of sustainability in the manufacturing process. Organic photovoltaics, for instance, often rely on halogenated solvents such as chloroform or chlorobenzene for their ability to easily dissolve blends of semiconducting polymers and small molecules. These halogenated solvents are broadly known to be toxic and exhibit a range of health and environmental hazards[131, 134, 172, 173]. Many reports of organic solar cells have highlighted the use of greener non-halogenated and non-aromatic solvents such as toluene, o-xylene, or tetrahydrofuran, demonstrating comparable device efficiencies to devices prepared from the standard halogenated solvent[19, 62, 129, 174–181]. However, when comparing these alternatives to standard halogenated

solvents they still fall short to meeting industrial standards for solvent safety.

4.1 Introduction to Organic Solvents

Organic solvents are used to dissolve organic semiconductor materials and prepare homogenous inks ready to be deposited with solution-based techniques. The ability to dissolve organic semiconductors in solvents allows for the creation of uniform thin films when the solution is deposited with spin-coating, inkjet printing, or blade-coating. The choice of solvent can significantly influence the morphology of the semiconductor film. The rate of solvent evaporation, solvent interactions with the semiconductor, and solvent polarity can all affect the crystallinity, phase separation, and molecular orientation within the film, which in turn impact the device performance. Many organic solvents are volatile, enabling the processing of organic semiconductors at relatively low temperatures compared to inorganic semiconductors. This is advantageous for flexible substrates and roll-to-roll manufacturing techniques. Solution processing with organic solvents can be more scalable and cost-effective compared to vacuum-based deposition techniques. Thus, a critical component of the advantages of organic semiconductors are contingent on proper solvent selection.

Examples of common organic solvents are aromatic solvents and halogenated (commonly chlorinated) solvents. These include toluene and xylene, frequently used with organic light emitting diodes, and chloroform and chlorobenzene, commonly used with organic photoabsorbing materials. Chemical structures of various solvents used with organic photovoltaic materials are shown in Figure 4.1.

Solvent selection can be a complex process weighing the toxicity of a solvent and the functional solubility of the solutes and solvents. The solubility parameter, which governs the compatibility between the solvent and the organic semiconductor material must be considered. Solvents with similar solubility parameters to the semiconductor material tend to dissolve it effectively, leading to improved film quality and device performance. However, molecular weight and self-aggregation may not be easily predicted by this solubility parameter. Additionally, solvent evaporation rate and boiling point can influence film formation and drying kinetics, affecting the final morphology and crystallinity of the deposited layers. The consideration of green solvents and the physical properties ultimately influencing the device performance is explored further in later chapters.

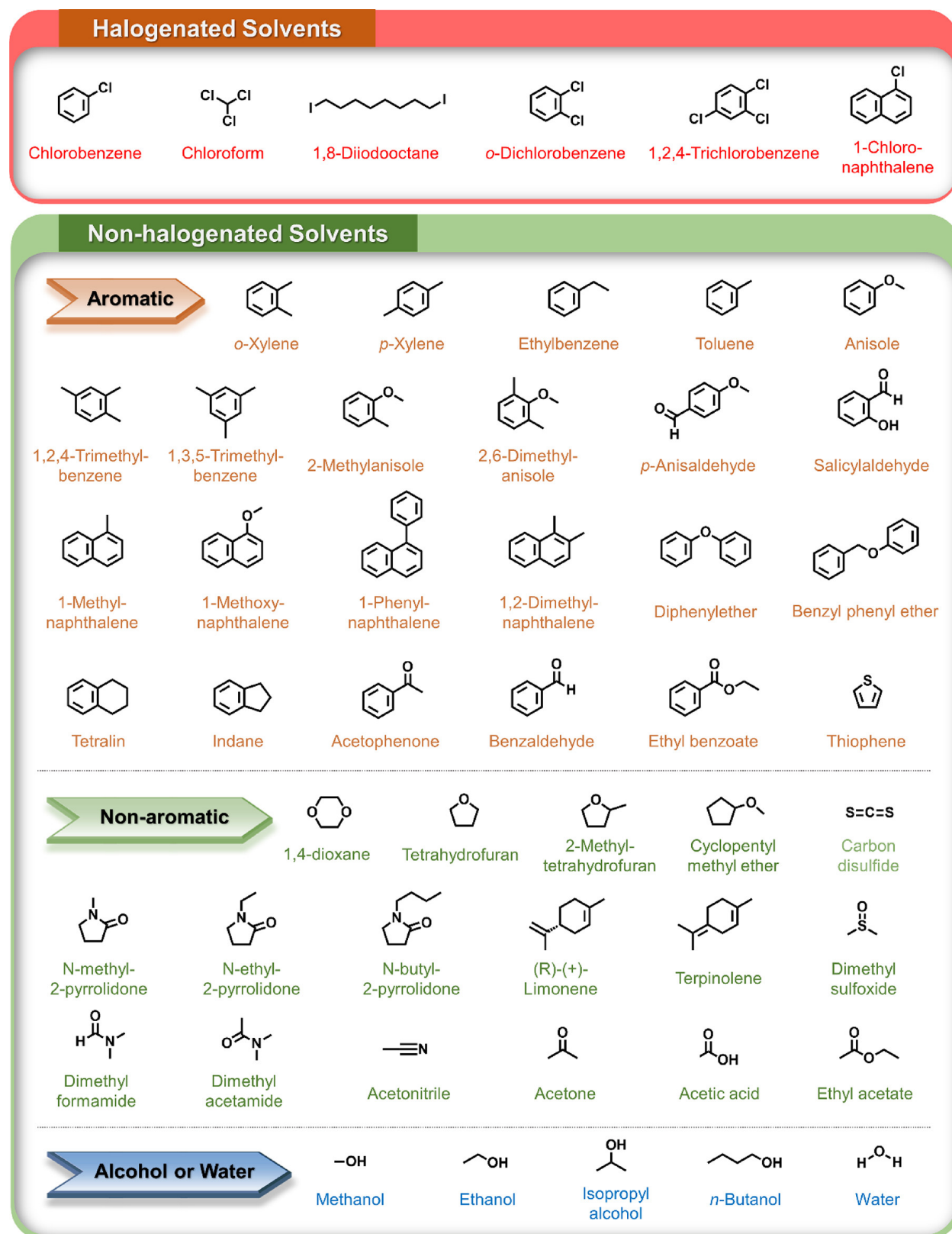


Figure 4.1: Chemical structures of representative halogenated and non-halogenated solvents used in organic photovoltaic fabrication. Figure from Lee (2020) [19]

4.2 Solvent Toxicities

4.2.1 Global Health and Safety (GHS)

The toxicity of solvents is commonly assessed through the Global Harmonized System of Classification and Labelling of Chemicals (GHS), a system that categorizes and labels hazards and toxicity found in laboratory settings and material safety data sheets (MSDS). The GHS pictograms, seen on chemical labels are shown in Figure 4.2. The GHS classifies hazards based on class and category, reflecting the nature and degree of the chemical product's hazard. Category 1 is the most severe while 4 is the least severe. For example, chloroform, a halogenated solvent widely used in organic electronics, falls under the GHS classification as a Category 2 carcinogen and a Category 2 reproductive toxin, indicating its potential to cause cancer and harm reproduction and fertility.



Figure 4.2: GHS pictograms used on labels to alert users of the chemical hazards to which they may be exposed. Each pictogram represents a distinct hazard.

It is widely acknowledged that halogenated and aromatic solvents should be replaced with alternatives whenever possible, as their use poses risks to both the environment and human health. This understanding is particularly emphasized in the literature on organic electronics, where discussions on “green solvent” research aim to find environmentally friendly alternatives. As shown in the Table 4.1, the commonly used solvents (chloroform, chlorobenzene, and o-dichlorobenzene) possess a long list of hazard statements. Thus, organic electronics literature often emphasizes replacement of halogenated and aromatic

solvents. However, this perspective may be incomplete. Examining two commonly proposed “green” solvents, toluene and tetrahydrofuran, as alternatives to chlorobenzene, a GHS comparison reveals that despite lacking halogenation or aromaticity, these solvents still possess a long list of hazards as seen in Table 4.2. This indicates that the hazards associated with certain solvents extend beyond halogenation and aromaticity, urging a more comprehensive evaluation of solvent safety.

GHS classifications provide broad categorizations of solvents; however, this may not adequately reflect real-world conditions or the specific applications in industrial settings. Industrial relevant factors include recyclability, waste disposal, storage procedures, exposure control and life cycle management. Therefore, it is crucial to conduct detailed risk assessments of solvent usage in industry relevant contexts.

4.2.2 Industry Solvent Selection Guides

Pharmaceutical companies commonly use organic solvents for chemical synthesis to improve reaction rates, product selectivity, lower mixture viscosity, and regulate temperatures of reactions. At least half of the materials used in drug synthesis production consists of solvents. As such, pharmaceutical companies have established selection guides as a tool for promoting use of green solvents in their processes. This includes GlaxoSmithKline (GSK), Pfizer, and Sanofi [132, 173]. Common factors that are considered include health hazard and exposure potential, flammability and reactivity, environmental impact, and disposability. GSK ranks sustainability in this manner, ranking solvents with a composite score G with 1 (least sustainable) to 10 (most sustainable). For instance, chlorobenzene and dichlorobenzene are both assigned a G score of 5.4, indicating a number of sustainability issues. An example decision tree for assigning the health score of a solvent is shown in Figure 4.3a. The decision tree considers the GHS H&P assignments, occupational exposure limits and the annual production levels of the solvent. Innovative Medicines Initiative (IMI)-CHEM21 public-private partnership is a European consortium published a selection guide for common solvents and ranked them by safety, health, and environmental criteria aligned with the Global Harmonized System (GHS) and other European regulations. While many organic solvents are ranked similarly amongst industry-relevant guides, there are minor discrepancies based on the ranking approach, application of use and primary operating regulations in the location of the organization. A summary of the solvents and various solvent ranking guides is shown in the table in Figure 4.3b where green represents preferred solvents, yellow represents solvents with some concerns, and red represents hazardous solvents that should be substituted.



Figure 4.3: a) GSK decision tree for determination of GHS Hazard and Precautionary (H&P) phrases for a given solvent. b) Example classification of common solvents by different industry solvent rankings. Figure adapted from Alder et al. (2016) and Byrne et al. (2016) [133, 173].

Table 4.1: Comparison of commonly used solvents with organic photoabsorbing materials.

Solvent	SDS Labels	Hazard Statements	GSK G	CHEM21
Chloroform	Irritant Toxic Carcinogens Extremely Hazardous Reproductive Toxins	H331 - Toxic if inhaled (Category 3)	4.4	Highly Hazardous
		H301 - Toxic if swallowed (Category 3)		
		H302 - Harmful if swallowed (Category 4)		
		H315 - Causes skin irritation (Category 2)		
		H319 - Causes serious eye irritation (Category 2A)		
		H336 - May cause drowsiness or dizziness (Category 3)		
		H335 - May cause respiratory irritation (Category 3)		
		H351 - Suspected of causing cancer (Category 2)		
		H372 - Causes damage to organs through prolonged or repeated exposure (Category 1)		
		H341 - Suspected of causing genetic defects (Category 2)		
Chlorobenzene	Irritant Flammable Toxic	H361 - Suspected of damaging fertility or the unborn child (Category 2)	5.4	Problematic
		H370 - Causes damage to organs (Category 1)		
		H402 - Harmful to aquatic life (Category 3)		
		H226 - Flammable liquid and vapour (Category 3)		
		H315 - Causes skin irritation (Category 2)		
o-Dichlorobenzene	Irritant Sensitizer Combustible Toxic Flammable	H332 - Harmful if inhaled (Category 4)	5.4	Problematic
		H411 - Toxic to aquatic life with long lasting effects (Category 2)		
		H401 - Toxic to aquatic life (Category 2)		
		H302 - Harmful if swallowed (Category 4)		
		H315 - Causes skin irritation (Category 2)		
		H317 - May cause an allergic skin reaction (Category 1)		
		H319 - Causes serious eye irritation (Category 2A)		
		H332 - Harmful if inhaled (Category 4)		
		H335 - May cause respiratory irritation (Category 3)		
		H400 - Very toxic to aquatic life (Category 1)		
		H410 - Very toxic to aquatic life with long lasting effects (Category 1)		
		H227 - Combustible liquid (Category 4)		

Notably, chlorobenzene and chloroform receive poor scores (“problematic” and “highly hazardous”) due to sustainability issues, as indicated by their environmental and health scores. Chlorobenzene, o-dichlorobenzene, and chloroform are consistently viewed as highly

toxic and undesired solvents. In addition, contrary to some perceptions in organic electronic literature, tetrahydrofuran and toluene, often touted as green solvents, are labeled as problematic in these guides (Table 4.2), suggesting nonaromatic and nonhalogenated solvents can still be undesirable for industrial manufacturing. This emphasizes the importance of aligning solvent choices with standardized criteria.

Table 4.2: Comparison of common “green” solvents reported in organic electronics literature. Many non-halogenated and non-aromatic solvents still possess a long list of hazards and low solvent guide rankings.

Solvent	SDS Labels	Hazard Statements	GSK G	CHEM21
Tetrahydrofuran (THF)	Peroxide Former Irritant Flammable Carcinogens	H225 - Highly Flammable liquid and vapour (Category 2)	4.8	Problematic
		H302 - Harmful if swallowed (Category 4)		
		H319 - Causes serious eye irritation (Category 2A)		
		H335 - May cause respiratory irritation (Category 3)		
		H351 - Suspected of causing cancer (Category 2)		
		H316 - Causes mild skin irritation (Category 3)		
O-xylene	Irritant Flammable Toxic	H226 - Flammable liquid and vapour (Category 3)	N/A	Problematic
		H312 - Harmful in contact with skin (Category 4)		
		H315 - Causes skin irritation (Category 2)		
		H319 - Causes serious eye irritation (Category 2A)		
		H332 - Harmful if inhaled (Category 4)		
		H335 - May cause respiratory irritation (Category 3)		
		H304 - May be fatal if swallowed and enters airways (Category 1)		
		H402 - Harmful to aquatic life (Category 3)		
Toluene	Irritant Flammable Toxic Reproductive Toxins	H412 - Harmful to aquatic life with long lasting effects (Category 3)	6	Problematic
		H225 - Highly Flammable liquid and vapour (Category 2)		
		H315 - Causes skin irritation (Category 2)		
		H336 - May cause drowsiness or dizziness (Category 3)		
		H304 - May be fatal if swallowed and enters airways (Category 1)		
		H361 - Suspected of damaging fertility or the unborn child (Category 2)		
		H373 - May cause damage to organs through prolonged or repeated exposure (Category 2)		
		H401 - Toxic to aquatic life (Category 2)		

4.3 Hansen Solubility Theory

In addition to safety and toxicity, or “greenness” considerations, solvent selection must also incorporate functionality. For many organic semiconductors, solvents are chosen for the ability to dissolve the semiconducting materials into a homogenous solution for deposition of the bulk heterojunction. The solubility of materials can be informed by the Hansen solubility theory, distilling the molecular interactions of molecules into three Hansen Solubility parameters (HSP)[143, 144, 182, 183]. Represented as a position in a three-dimensional space, the HSP of a solvent is a measure of the cohesive energy of that solvent, or the amount of energy required to vaporize the solvent, which is represented by the intermolecular interactions: dispersion δD , polar δP and hydrogen bonding δH . The theory is utilized by visualizing the HSP distance between two molecules, R_a .

$$R_a^2 = 4(\delta_{D_1} - \delta_{D_2})^2 + (\delta_{P_1} - \delta_{P_2})^2 + (\delta_{H_1} - \delta_{H_2})^2 \quad (4.1)$$

The scalar 4 in front of the dispersion component of the equation is a weighting factor. Dipolar and hydrogen bonds are directional and form stable pairs, reducing their interaction with surrounding molecules, which reduces the effective interactions by half. Since the solubility parameter is the square root of the cohesive energy density, the factor $\frac{1}{4}$ would appear for the dipolar and hydrogen bonding terms. Finally, rather than using fractions, a factor of 4 is used to weight the dispersive component.

The smaller the R_a between two solvents, the more alike the two solvents are and the more the solvents are interchangeable in the solute-solvent system. Similarly, solutes are characterized by their HSP values, which represent their ability to participate in these different types of interactions. By comparing the HSP values of solvents and solutes, one can predict whether they will mix well and form a stable solution. The Hansen Solubility Theory is often referenced when looking for alternative solvents for solution processable material systems spanning from materials science, pharmaceuticals, and electronics. Along with hazard analysis and industry-relevant selection criteria, the Hansen Solubility Theory can provide a starting point for finding suitable green solvent alternatives.

The solubility characteristic of the solvent can be simplified to the relative energy difference (RED) number where value greater than 1 is a poor solvent and value less than 1 is a good solvent.

$$\text{RED} = \frac{R_a}{R_o} = \frac{\text{distance from sphere center}}{\text{sphere radius}} \quad (4.2)$$

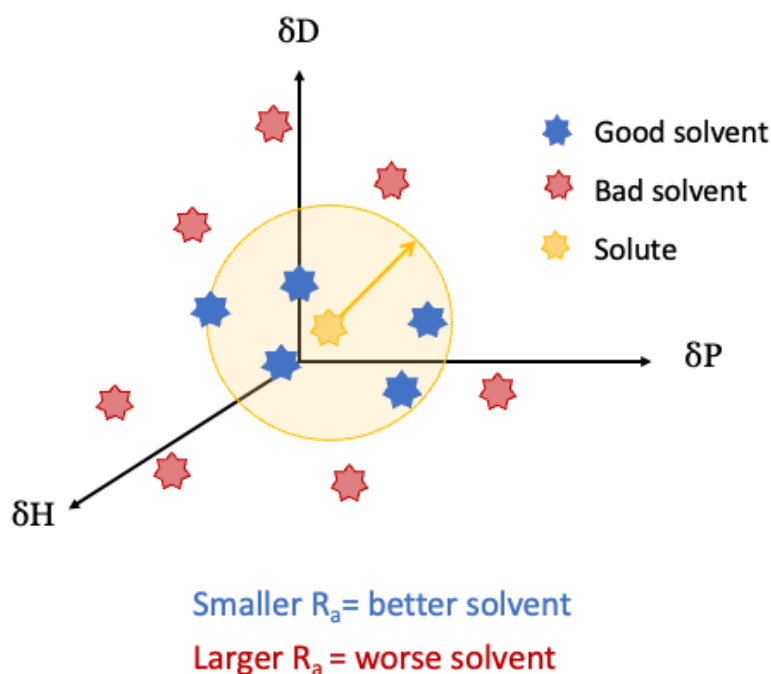


Figure 4.4: Visualization of the Hansen Solubility Space with a solubility sphere highlighted in yellow. The radius, R_a is shown as the yellow arrow with the solute at the center. Good solvents fall within this sphere and bad solvents exist outside of this sphere.

HSP of common molecules and solvents can be found through reported literature or datasets online. These values have been calculated with equations developed through a series of contributions from Blanks and Prausnitz, Beerbower, and Bottcher, considering molar volume, vector sum of dipole moments, refractive indices, and dielectric constants[143]. For more complex molecules or polymers, the HSP can be empirically found through the binary solvent gradient method proposed by Machui et al. in 2012 [182]. The method utilizes mixtures of a solvents as a means of exploring the HSP space where the solvents are chosen based on dominate contribution to a single coordinate in space (hydrogen, polar, or disperse). A solubility threshold is chosen to bin solvent compositions as good or bad solvents. A higher solubility threshold requires a higher concentration of solute to be properly dissolved, and thus results in fewer solvents classified as good solvents. A fitting routine is used to find the resulting solubility sphere in which the center of such sphere is defined as the HSP of the tested molecule.

Although HSP theory provides a good framework for solvent selection, it does not necessarily guarantee a proper dissolution in reality. Functionality of the solvent will depend on the physical properties of the material of interest. Additionally, newer solubility theories have been proposed to address several issues with HSP theory and improve methods for determining the solubility of new materials with much more complex chemical functionalities. These include Convex Solubility Parameters (CSP) and the Functional Solubility Approach[145, 146]. While interesting, these approaches or models are out of scope for this work. The next chapters discuss the results of investigating the use of green solvents for organic photovoltaics.

Chapter 5

Green Solvent Processed Organic Solar Cells

Advances in OPVs have enabled solution-processable solar cells with competitive PCEs and the potential for scalable manufacturing. However, the fabrication process of record-performing organic solar cells utilize highly toxic solvents that pose environmental and human hazards, limiting their ease of fabrication. This chapter proposes greener solvents guided by industry-relevant selection rankings. Evaluating the compatibility of different photovoltaic materials and greener solvents, this chapter presents steps towards using a single host solvent in processing OPVs in a conventional device architecture. GSK and CHEM21 selection guides are used. While there are examples of nonhalogenated or nonaromatic solvents with lower R_a values studied in literature, this approach emphasizes solvent safety first. From this analysis, one green solvent is selected to demonstrate steps towards optimizing film characteristics and device parameters of solution-processed organic solar cells.

5.1 Materials System Compatibility

The solvents considered in this work (Ani, MIBK, EA) have few GHS hazards compared to chlorinated solvents, have a GSK G score greater than or equal to 6.5, and are “recommended” by industry-relevant selection guides. Qualifying greener solvents with a range of solubility parameters are listed in Table 5.1. The solubility distance is calculated below as the distance between chlorobenzene and an alternative solvent ($R_{a,CB-solv}$) in the equation below with the individual HSP listed in Table 5.2.

$$R_{a,CB-solv}^2 = 4(\delta_{D,CB} - \delta_{D,solv})^2 + (\delta_{P,CB} - \delta_{P,solv})^2 + (\delta_{H,CB} - \delta_{H,solv})^2 \quad (5.1)$$

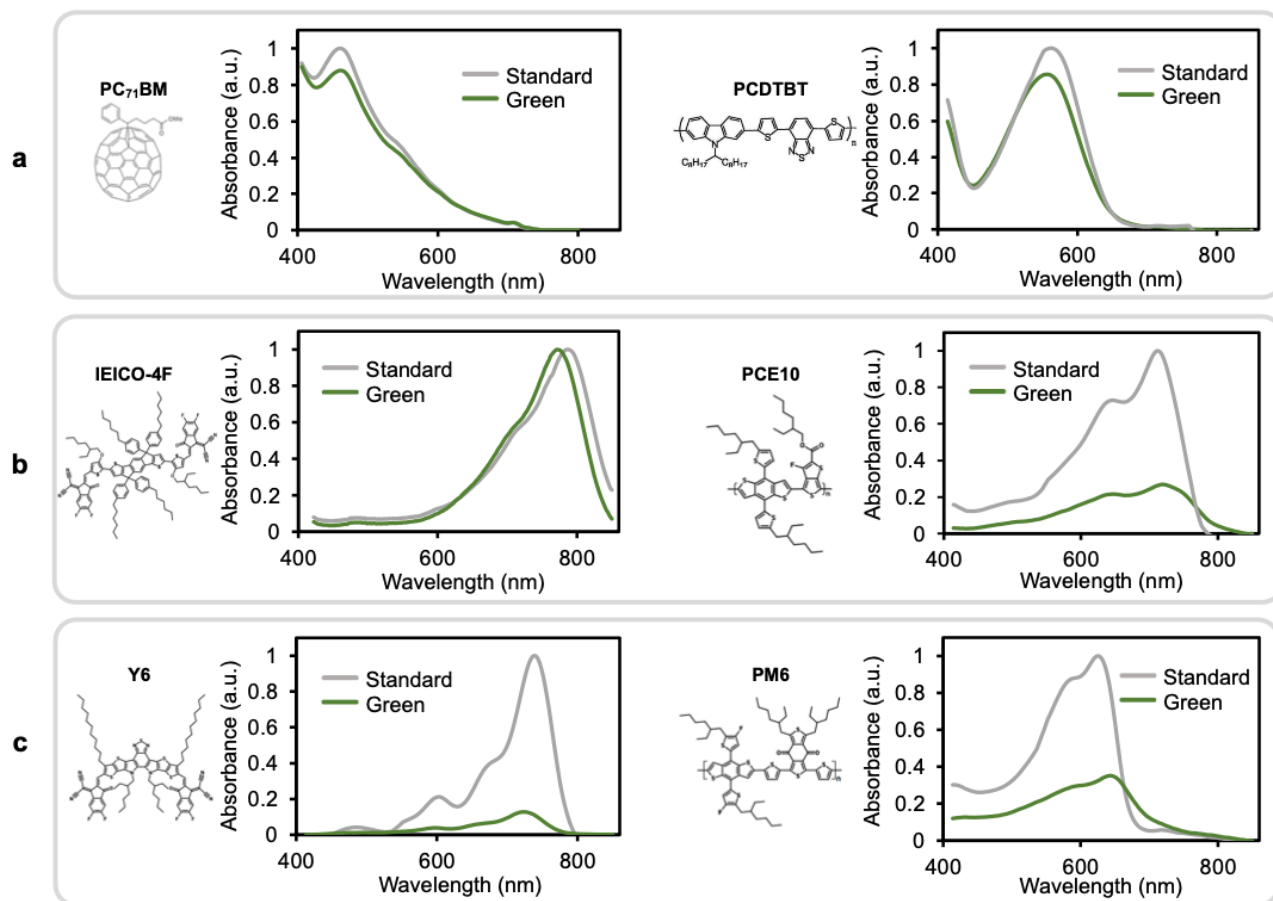
Table 5.1: Properties of green solvents investigated in this work

Solvent	SDS Labels	Hazard Statements	GSK G	CHEM21
Anisole	Irritant	H226 - Flammable liquid and vapour (Category 3)	7.4	Recommended
	Combustible	H303 - May be harmful if swallowed (Category 5)		
	Flammable	H401 - Toxic to aquatic life (Category 2)		
Methyl Isobutyl Ketone (MIBK)	Irritant Flammable	H225 - Highly Flammable liquid and vapour (Category 2)	6.5	Recommended
		H319 - Causes serious eye irritation (Category 2A)		
		H336 - May cause drowsiness or dizziness (Category 3)		
		H303 - May be harmful if swallowed (Category 5)		
		H333 - May be harmful if inhaled (Category 5)		
Ethyl Acetate	Irritant Flammable	H225 - Highly flammable liquid and vapor (Category 2)	6.7	Recommended
		H319 - Causes serious eye irritation (Category 2A)		
		H336 - May cause drowsiness or dizziness (Category 3)		

Starting with the smallest R_a solvent, anisole (Ani), we study the solubility of common OPV material sets with this greener solvent compared to (CB) or chloroform (CF). The OPV donors and acceptors studied were: PCDTBT, PC₇₁BM, PCE10, IEICO-4F, PM6, and Y6 (full chemical names in Table A.1). Solutions of each material were first prepared using a concentration of 20 mg mL⁻¹, heated and stirred, then filtered with a glass microfiber filter to remove undissolved particulates. The UV-Vis absorption spectrum of each filtered solution is then obtained and shown in Figure 5.1. Overall, absorbance spectra are lower in the anisole solutions than in the chlorinated solutions due to its larger R_a . When the materials are prepared in greener solvents, a limited amount of semiconductor material is fully dissolved. Consequently, when the undissolved material is filtered away, the final solution is less concentrated with photo-absorbing material, resulting in lower measured absorption. Although the two materials systems PCE10:IEICO-4F and PM6:Y6 are highly sought for their high PCEs in OPVs, the lower absorption profiles indicate low solubility in anisole, the smallest R_a solvent proposed here. Based on HSP theory, it is expected that the solubility of PCE10:IEICO-4F and PM6:Y6 would be even lower in the larger R_a solvents in Table 1. However, both the PCDTBT donor and PC₇₁BM acceptor exhibit similar absorption in the greener solvent versus the chlorinated solvent. This suggests that PCDTBT:PC₇₁BM would be a good choice to investigate the impact of solvent selection on processing OPVs.

Table 5.2: CAS Numbers and Hansen Solubility Parameters of investigated solvents considered in this work.

Solvent	CAS	dD	dP	dH
Chlorobenzene	108-90-7	19	4.3	2
Anisole	100-66-3	17.8	4.4	6.9
Methyl Isobutyl Ketone (MIBK)	108-10-1	15.3	6.1	4.1
Ethyl Acetate	141-78-6	15.8	5.3	7.2

Figure 5.1: Absorption spectrum of various acceptor and donor material systems dissolved in standard chlorinated solvents and the greener solvent, anisole (Ani). Standard solvents used were chlorobenzene (CB) for PCDTBT:PC₇₁BM and PCE10:IEICO-4F systems and chloroform (CF) for the PM6:Y6 system.

5.2 Greener Solvent Selection

The solvents from Table 5.2 were evaluated with PCDTBT:PC₇₁BM to correlate HSPs with the functional solubility of the blend system in greener solvents. A total of 20 mg of PCDTBT:PC₇₁BM material was prepared in a 1:3 ratio and dissolved in 1 mL of Ani, MIBK, and EA. Each solution was heated and stirred at 70 °C for at least 4 hours on a hotplate then filtered. Figure 5.2 shows the images and UV-Vis absorbance profiles of the resulting solutions. Consistent with Hansen Solubility Theory, as R_a increased, the less compatible the material is in the solvent and the lower the final concentration of absorber was. The images show that the blended solutions are visibly lighter as R_a increases, indicating lower concentrations of dissolved photo-absorbing semiconductor in solution. Absorption values indicate that the greener solutions exhibit lower concentrations than the chlorobenzene solution. Furthermore, MIBK and EA solutions exhibit 200 times lower absorption intensity, particularly in the wavelength range between 550 to 700 nm.

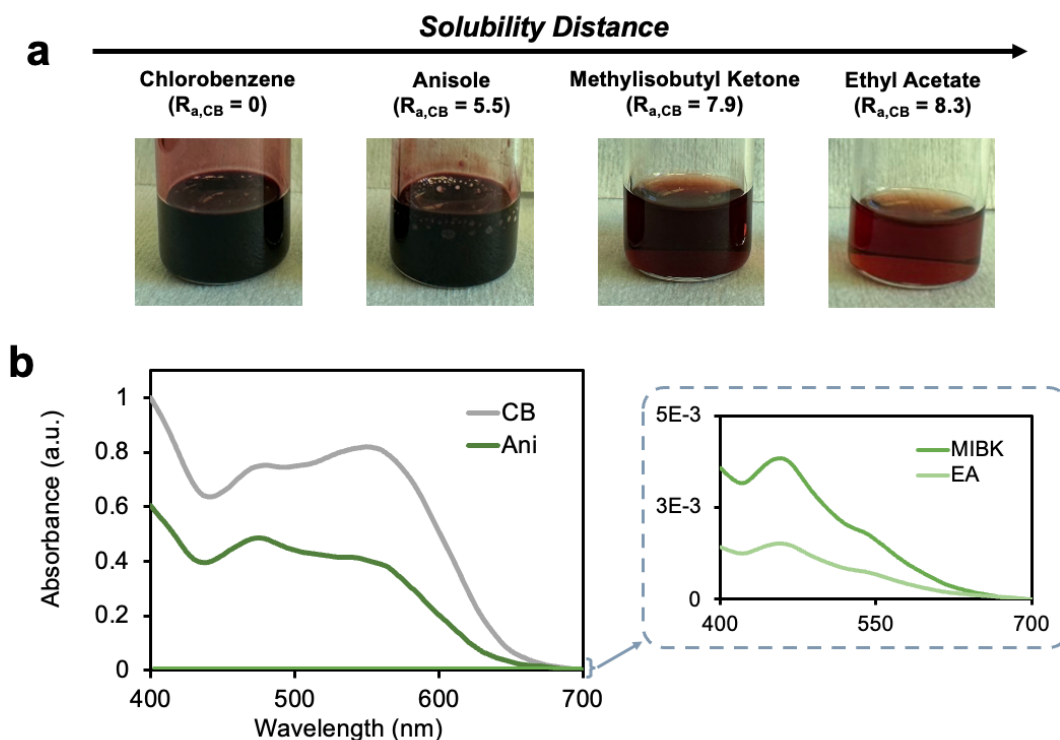


Figure 5.2: (a, b) Images and absorbance spectra of filtered PCDTBT:PC₇₁BM blends prepared in the host solvents: chlorobenzene (CB), anisole (Ani), methyl isobutyl ketone (MIBK), and ethyl acetate (EA).

Table 5.3: Wavelengths of peak absorption for each PCDTBT only or PC₇₁BM only solution.

Solvent	R_a	PCDTBT (nm)	PC ₇₁ BM (nm)
Chlorobenzene (CB)	0	563	463
Anisole (Ani)	5.5	552	462
Methyl Isobutyl Ketone (MIBK)	7.9	538	458
Ethyl Acetate (EA)	8.3	519	458

PCDTBT donor and PC₇₁BM acceptor solutions were prepared individually in the same method described above. UV-Vis absorbance was measured after filtration. Figure 5.3 shows the images and UV-Vis absorbance spectrum of the solutions. The images (Figure 5.3a) show that concentration decreases with increasing R_a for both PCDTBT donor and PC₇₁BM acceptor solutions, consistent with Hansen Solubility Theory. This is confirmed by absorbance spectrum where concentration of PCDTBT and PC₇₁BM decreases with increasing R_a of the solvent (Figure 5.3bc and ef). Analysis of the normalized absorbance spectra of all PCDTBT solutions show that the peak absorbance wavelength (λ_{max}) provides another indicator of increased R_a (Figure 5.3d). The peak absorbance position is listed in Table 5.3, showing that increased R_a leads to blue shifts in λ_{max} . This is attributed to the solvatochromic effect where the larger R_a of the greener solvents induce a hypsochromic shift in the absorption profile [184]. This manifests in as much as a 25 nm peak shift between the CB and MIBK solutions for PCDTBT solutions. However, solvatochromism is not observed in the PC₇₁BM solutions (Figure 5.3g). This is expected as the solvatochromic phenomenon is attributed to the π - π stacking of conjugated π -electron systems and is influenced by solvent polarities. Thus, it is observed with the polymer donor PCDTBT and not the small molecule PC₇₁BM.

Of the greener solvents investigated, anisole showed the most compatibility with the PCDTBT:PC₇₁BM material system. Our solvent analysis is consistent with previous studies where an R_a of 6 was typically the threshold between good and poor solvents[183]. Previous literature using anisole as the host solvent for OPV devices have reported PCEs up to 4.5% using molecular design approaches to enhance the solubility of the polymer donor [35, 185, 186]. The synthesized conjugated polymers have been shown to produce higher performing OPVs when processed with anisole than with chlorinated solvents. However, the greener processed OPVs with synthesized derivatives still do not meet PCEs of the original blends with chlorinated solvents without solvent additives. Here, we further proceed with the use of anisole as a single host solvent for investigating greener processed PCDTBT:PC₇₁BM organic solar cells.

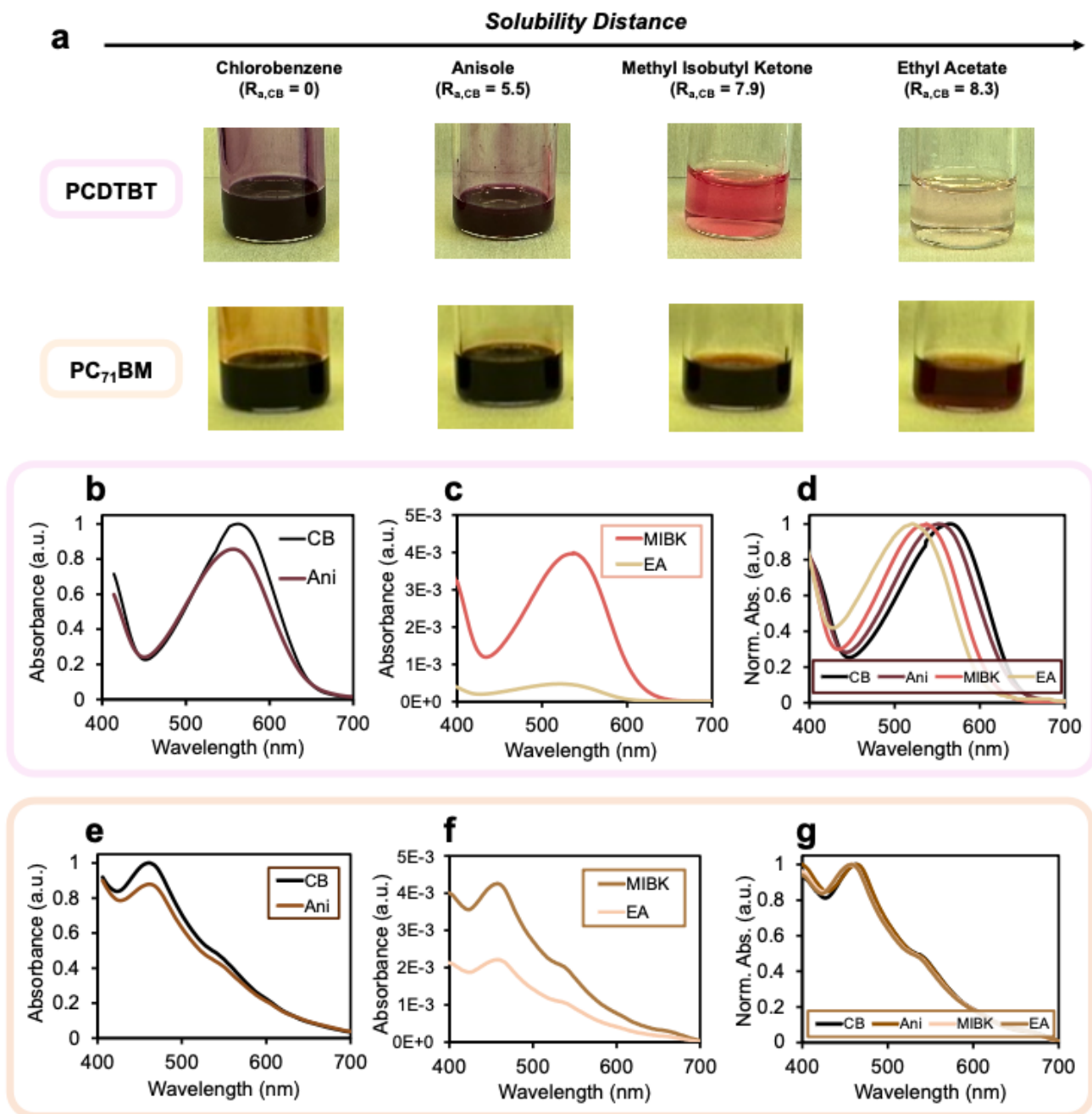


Figure 5.3: (a) Images of filtered donor only and acceptor only solutions dissolved in chlorobenzene and anisole. **PCDTBT only solutions:** (b, c) Absorbance spectra of PCDTBT dissolved in various host solvents after filtration. (d) Normalized absorbance spectra of the same PCDTBT solutions overlayed to show solvatochromatism. **PC₇₁BM only solutions:** (e, f) Absorbance spectra of PC₇₁BM dissolved in various host solvents after filtration. (g) Normalized absorbance spectra of same PC₇₁BM solutions overlayed.

5.3 Device Fabrication

OPV devices were fabricated from two solutions were prepared by loading 20 mg of 1:3 PCDTBT:PC₇₁BM in 1 mL of either chlorobenzene or anisole. After heating and stirring, the two solutions were filtered and used in spin-coating conventional OPVs. Figure 5.4 shows the solution absorbance, film absorbance and device characteristics obtained using the chlorobenzene and anisole solutions. Compared to the chlorobenzene solution, the anisole solution exhibited a lower absorption, indicating a lower overall solution concentration as discussed previously (Figure 5.4a). As a result, the spun anisole film is thinner and less absorbing than the chlorobenzene film (Figure 5.4b). Because photon penetration depth increases with increasing wavelength, thinner films will exhibit lower efficiencies at longer wavelengths. Consequently, the anisole devices exhibit a steeper drop off in external quantum efficiency (EQE) at longer wavelengths and worse PCEs overall compared to chlorobenzene devices (Figure 4c and d). The OPV characteristics are listed in Table 5.4. From this initial comparison, anisole cannot simply replace chlorobenzene in preparing the OPV solution, and further solution optimization is needed.

Table 5.4: Device characteristics of solar cells fabricated from filtered chlorobenzene and anisole solutions.

Solvent	Loaded Mass	PCE (%)	FF (%)	Jsc (mA cm ⁻²)	Voc (V)
Chlorobenzene	20 mg	4.76 ± 0.10	56.0 ± 0.6	9.7 ± 0.1	0.88 ± 0.01
Anisole	20 mg	1.68 ± 0.15	47.6 ± 1.2	4.4 ± 0.2	0.81 ± 0.01

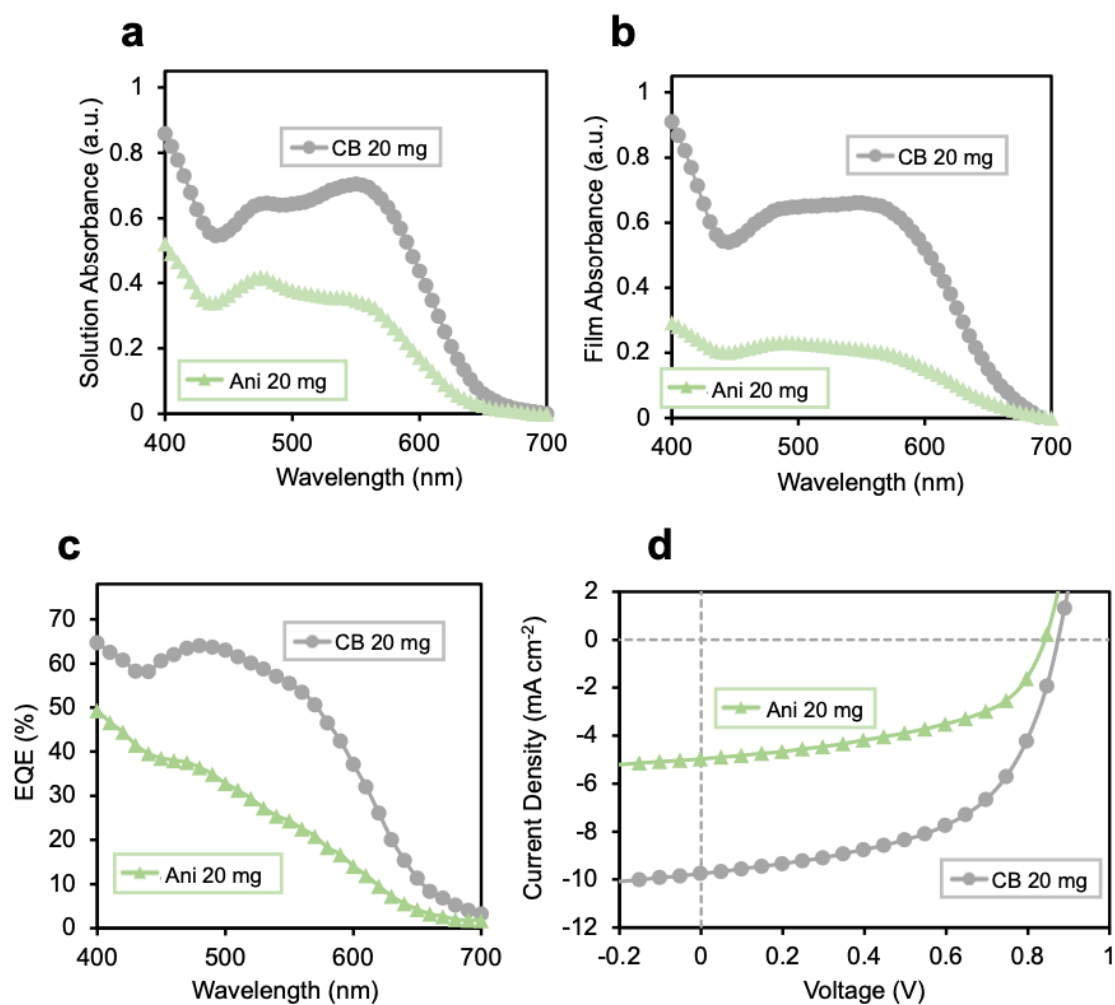


Figure 5.4: OPV solution blends were prepared with a starting mass of 20 mg in 1 mL of solvent. (a, b) Absorbance spectrum of the filtered solution and the corresponding spin-coated film. (c, d) External quantum efficiencies and current density-voltage characteristics of devices prepared from the solutions.

5.4 Optimizations for Solution Concentration

To address the low solution concentration and resulting thin active films when OPVs are processed with anisole, a higher concentration solution was prepared with a mass load of 40 mg. After heating, stirring and filtering, the solution concentration increased to better match that of the original 20 mg chlorobenzene solution (Figure 5.5). Additionally, the 40 mg anisole solution viscosity was measured to be 1.82 cP, closer to the 1.77 cP of the 20 mg chlorobenzene blend.

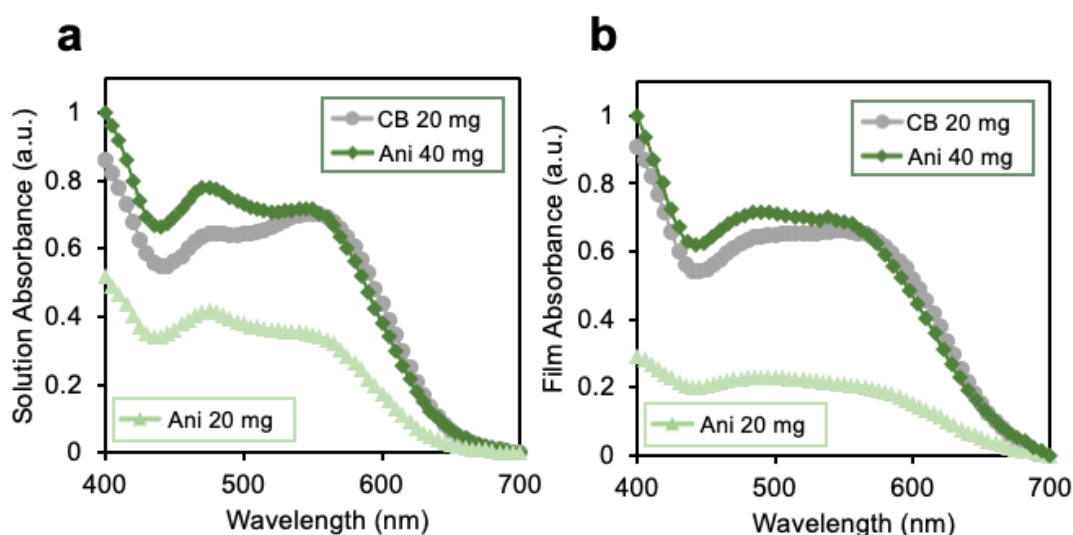


Figure 5.5: Absorption spectra comparing chlorobenzene 20 mg, anisole 40 mg, and anisole 20mg (a) solutions and (b) films.

As a comparison, we also investigate a “composition-matched” solution blend where the anisole solution’s donor/acceptor ratio is identical to that of the chlorobenzene solution. Previously, the dry donor and acceptor semiconductor materials are combined prior to adding the desired solvent. However, differences in solubility between the donor and acceptor materials in greener solvents can lead to undesired changes in the final solution composition. For instance, the different absorbance topologies of the 20 mg chlorobenzene solution versus 40 mg anisole solution are seen in Figure 5.5a. The absorption values at the peak wavelengths (560 nm for PCDTBT donor and 460 nm for PC₇₁BM acceptor) indicate that anisole solution does not possess the same donor/acceptor composition as the chlorobenzene solution. For the composition matched solution blend, donor and acceptor materials are dissolved individually, concentration measured with UV-Vis absorbance, then combined to form the blend. This guarantees the correct donor/acceptor composition is prepared in the final

solution. Figure 5.6 illustrates the steps necessary to achieve composition in a greener solvent matching that of the chlorinated solvent. Individual donor and acceptor solutions are prepared by heating, stirring, and filtering the solutions separately with the greener and chlorinated solvent. Absorbance spectra of individual donor and acceptor solutions are measured. The concentration of each greener donor and acceptor solution is then evaluated by comparing its absorbance to the respective chlorinated solution. Finally, the desired greener solution blend is mixed according to dilution equations.

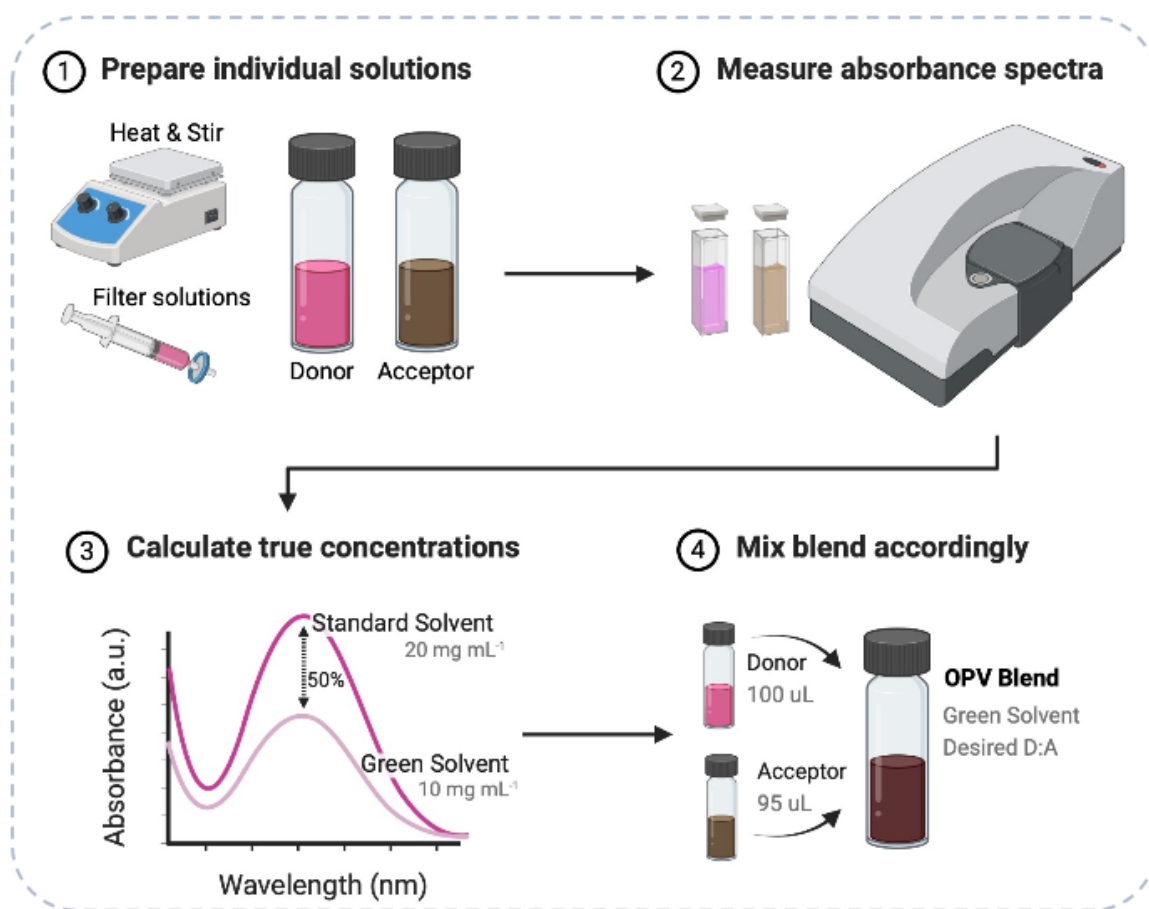


Figure 5.6: Illustration of steps to achieve a composition matched OPV blend with a green solvent. Created with BioRender.com.

Using the steps described (more details in the Appendix), a composition-matched anisole blend was prepared. The individual donor and acceptor solutions were prepared with anisole and chlorobenzene. Figure 5.7 shows the absorbance spectrum of filtered PCDTBT and PC₇₁BM solutions. To achieve the desired 1:3 donor/acceptor ratio when

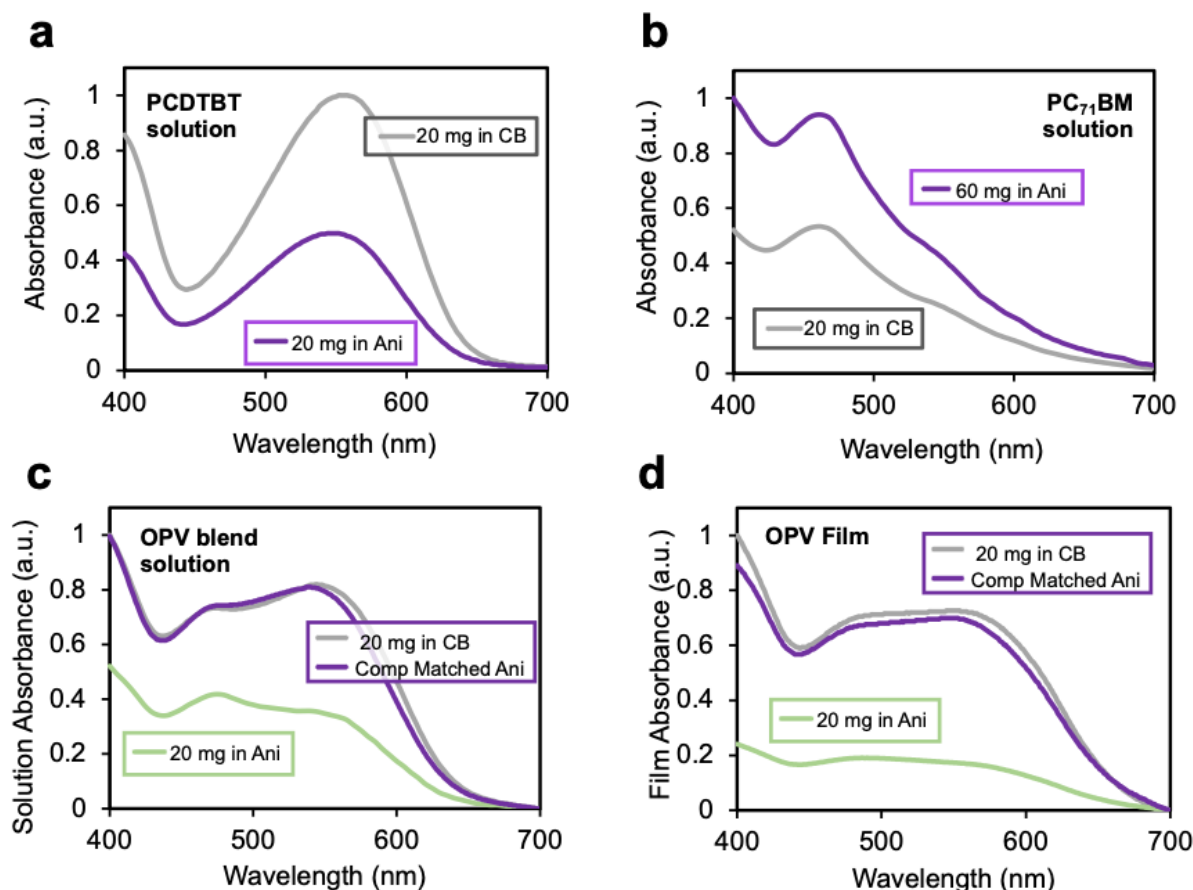


Figure 5.7: (a) Absorbance spectra of filtered solutions prepared with 20 mg PCDTBT loaded in chlorobenzene and anisole (b) Absorbance spectra of filtered solutions prepared from 20 mg loaded in chlorobenzene and 60 mg PC₇₁BM loaded in anisole. (c) Absorbance spectra of filtered solutions comparing 20 mg of 1:3 PCDTBT:PC₇₁BM loaded in anisole, 20 mg of 1:3 PCDTBT:PC₇₁BM loaded chlorobenzene, and the solution blend mixed from anisole solutions from a and b. (d) Absorbance spectra of OPV films prepared from the solutions in described in c.

combined, the PC₇₁BM mass loaded in anisole was increased to 60 mg. Table 5.5 shows the measured concentrations of individual anisole solutions when using chlorobenzene solutions as a reference. Using equations ?? and A.2, vol_A , vol_D , and $conc_{tot}$ were calculated. The absorbance spectrum of the new blended anisole solution closely matched both the composition (absorbance profile) and concentration (intensity) of the chlorobenzene solution as seen in Figure 5.7c and d.

Table 5.5: Measured concentrations of anisole solutions with increased acceptor mass.

Material	Loaded Mass	Measured Concentration
PCDTBT	20 mg	9.1 mg mL ⁻¹
PC ₇₁ BM	60 mg	35.2 mg mL ⁻¹

Volumes: if $\text{vol}_A = 1$, $\text{vol}_D = 0.78$

Calculated Total Concentration: 20.5 mg mL⁻¹

OPVs were spin-coated from both the 40 mg anisole solution and composition matched solution. The EQE and JV characteristics are shown in Figure 5.8a and b. The solar cell characteristics compared to previous devices are shown in Table 5.6 with a box plot of PCEs shown in Figure 5.9. Both anisole processed devices exhibit significantly improved performance when compared to the initial 20 mg anisole blend. The EQE characteristics of these anisole devices increased, nearly matching that of the initial 20 mg chlorobenzene solution. This can be attributed to the thicker photo-absorbing film enabled by the increased solution concentrations. Additionally, open-circuit voltage, short-circuit current, and fill-factors increased with the optimized anisole solutions leading to efficiencies of 4.08% and 4.17% compared to the 4.76% of the chlorobenzene devices.

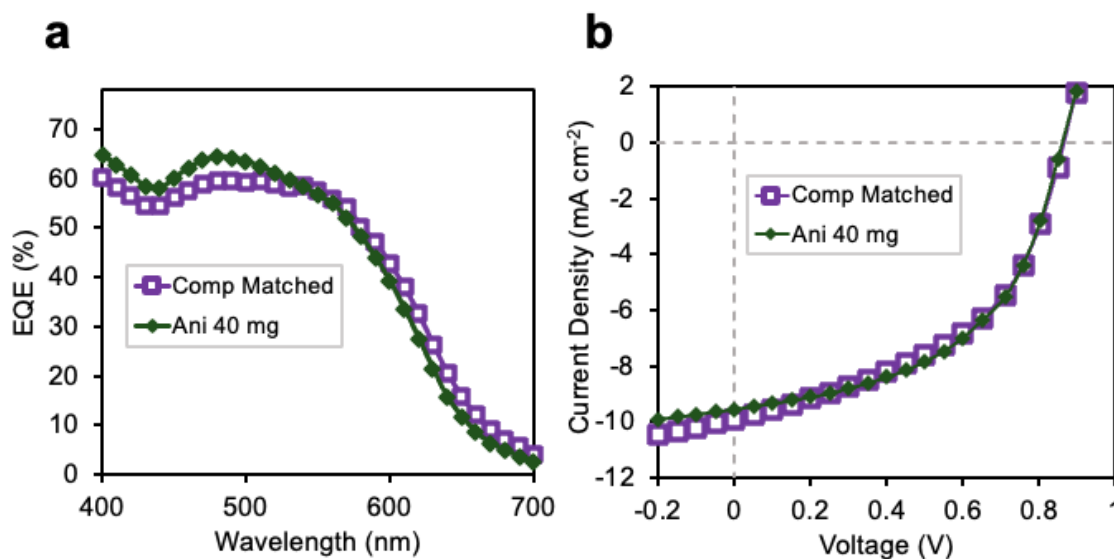


Figure 5.8: (a) External quantum efficiencies and (b) current density-voltage characteristics of 40 mg anisole devices and composition matched devices.

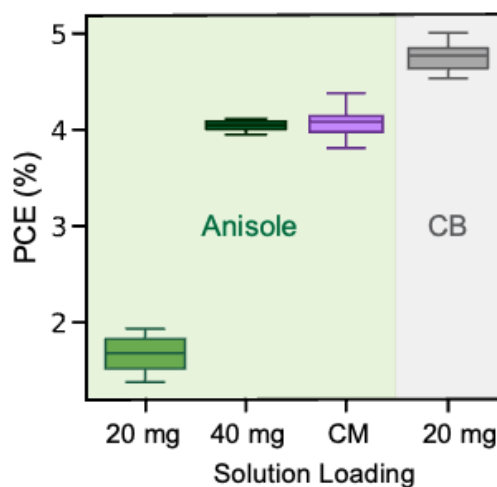


Figure 5.9: A comparison of power conversion efficiencies for devices spin-coated with 20 mg anisole blend, 40 mg anisole blend, composition matched anisole blend and 20 mg chlorobenzene blend.

Table 5.6: Median and half interquartile ranges of OPV devices spin-coated with chlorobenzene and anisole solutions.

Solvent	Solution	PCE (%)	FF (%)	Jsc (mA cm-2)	Voc (V)
Chlorobenzene	20 mg	4.76 ± 0.10	56.0 ± 0.6	9.7 ± 0.1	0.88 ± 0.01
Anisole	20 mg	1.68 ± 0.15	47.6 ± 1.2	4.4 ± 0.2	0.81 ± 0.01
	CM	4.08 ± 0.01	47.9 ± 0.7	9.8 ± 0.2	0.86 ± 0.0
	40 mg	4.17 ± 0.04	52.0 ± 0.5	9.5 ± 0.2	0.86 ± 0.0

The improved device characteristics can also be attributed to improved film crystallinity as seen through grazing incidence wide angle X-ray scattering (GIWAXS) measurements. Figure 5.10a and b shows the GIWAXS 2D images comparing 20 mg to 40 mg anisole films. Peaks are observed at positions around $q_z = 0.7, 1.3 \text{ \AA}^{-1}$ and $q_{x-y} = 0.3, 0.6, \text{ and } 1.3 \text{ \AA}^{-1}$ as shown in the line profiles. PC₇₁BM is known to dominate GIWAXS in blend films as PCDTBT is known to be largely amorphous[187, 188]. Thus, it is difficult to assess if the scattering can be attributed to the PCDTBT π - π stacking. Overall, however, 2D GIWAXS images show improved signal intensity from broad rings when moving from 20 mg to 40 mg films, suggesting improved crystallization within the film. This is consistent with the increased device efficiency in the 40 mg anisole device. These results emphasize the need to optimize solution blends when using greener solvents.

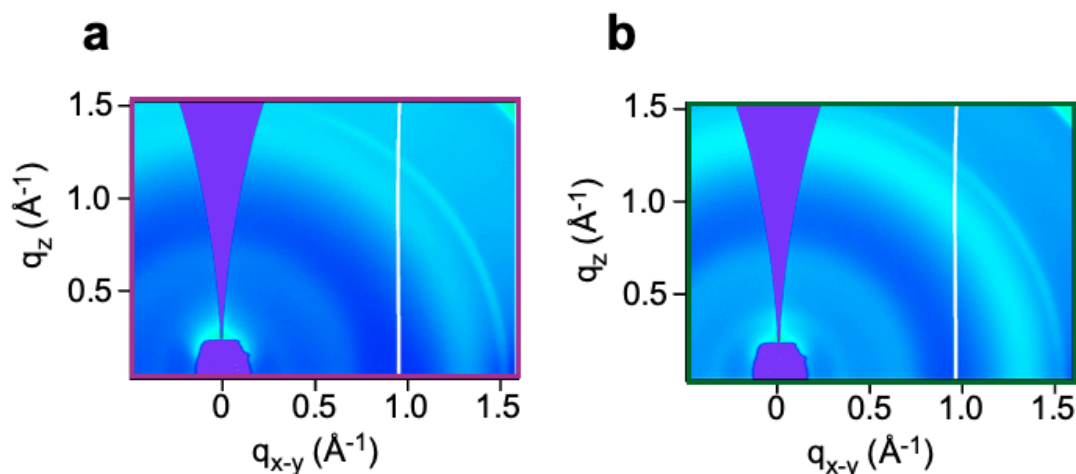


Figure 5.10: GIWAXS 2D images of spin-coated OPV films prepared from (a) 20 mg and (b) 40 mg anisole solutions.

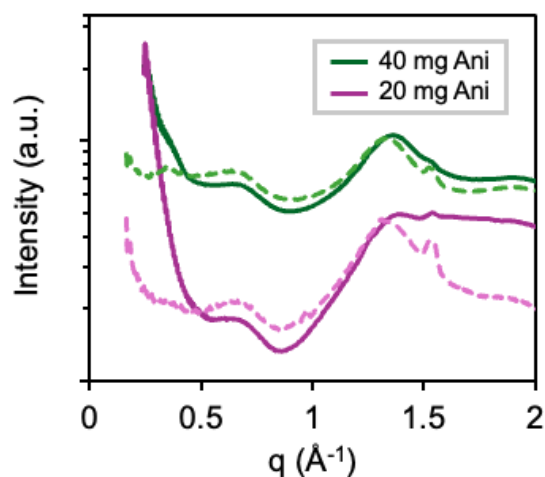


Figure 5.11: GIWAXS out-of-plane (solid) and in-plane (dashed) line profiles of films spin-coated OPV films prepared from (a) 20 mg and (b) 40 mg anisole solutions.

Here, anisole devices fall short of meeting the efficiency of chlorobenzene-based devices primarily due to lower fill factors. Although the concentrations and compositions are closely matched to the standard chlorobenzene solution, the limited efficiency suggests other solute-solvent factors may still impact the final film morphology. For instance, the anisole solutions and films still exhibit hypsochromic shifts in the donor absorption (550 nm). The blue

shift suggests reduced polymer aggregation within the solution compared to the standard solution, likely negatively impacting the molecular organization within the final film. In addition, the solvatochromic behavior arises from a shift in the energy bands which may be a factor impacting the charge transfer in addition to absorption. Thus, the maximum device performance using a larger R_a solvent such as anisole is limited due to its limited compatibility with organic semiconductor molecules. To our knowledge, the limitations of using large R_a solvents such as anisole has not been discussed in literature primarily due to a preference for using lower R_a solvents such as toluene, o-xylene, and tetrahydrofuran. Further investigations are necessary to fully elucidate the relationship between low solubility solutions and film formation in bulk heterojunction devices in an effort to expand the available solvents used in green processed devices.

5.5 Process Optimization

Beyond solution preparations, film processing is also critical in optimizing the final film morphology. Due to the higher boiling point of the anisole solvent compared to chlorobenzene (154 °C versus 132 °C), the drying times of spin-coated devices are expected to increase. In-situ UV-Vis measurements of films processed with chlorobenzene and anisole solutions were measured during spin-coating (Figure 5.12a and b). The solidification from wet solution to a thin film occurs when absorption peaks of the donor (560 nm) and acceptor (460 nm) broaden and eventually merge as seen in static film absorption profiles. Compared to the chlorobenzene film where donor and acceptor peaks plateau, the anisole film exhibits a more prominent acceptor absorption, coinciding with the EQE performance seen previously. This can be attributed to a lower solubility limit of PCDTBT donor in anisole relative to that in chlorobenzene. As a result of the proportionally lower PCDTBT content in the anisole blend, there is a steeper drop off in the donor's associated absorption beyond about 600 nm. The drying time, the time it takes for the film's UV-Vis absorbance intensity to stop changing, is extracted for each measurement and shown in Figure 5.13. The drying times for the 20 mg chlorobenzene solutions were shorter, at 5 seconds and 3 seconds for 1000 rpm and 1500 rpm, respectively. In contrast, the 40 mg anisole solutions took longer to dry, at approximately 20 seconds for both spin speeds. Although the increased airflow of faster spin rates may increase volume ejection and increase overall drying, we observe solvent volatility is a more critical parameter affecting drying time compared to spin rate.

The longer drying times of anisole may enable morphology to coarsen, domain sizes to grow, and phase separation to progress. An additional thermal annealing can be employed to both encourage nanoscale crystallization and accelerate film drying to confine the morphology [32, 189, 190]. To evaluate this, OPVs were spun with 40 mg anisole solutions and thermally annealed on a 70 °C hotplate for 10 minutes. GIWAXS 2D images and AFM images of these anisole films as spun and post-annealed were measured. Figure 5.14, Table 5.7, 5.15, and 5.16 shows the device characteristics, AFM topology, and GIWAXS 2D images comparing

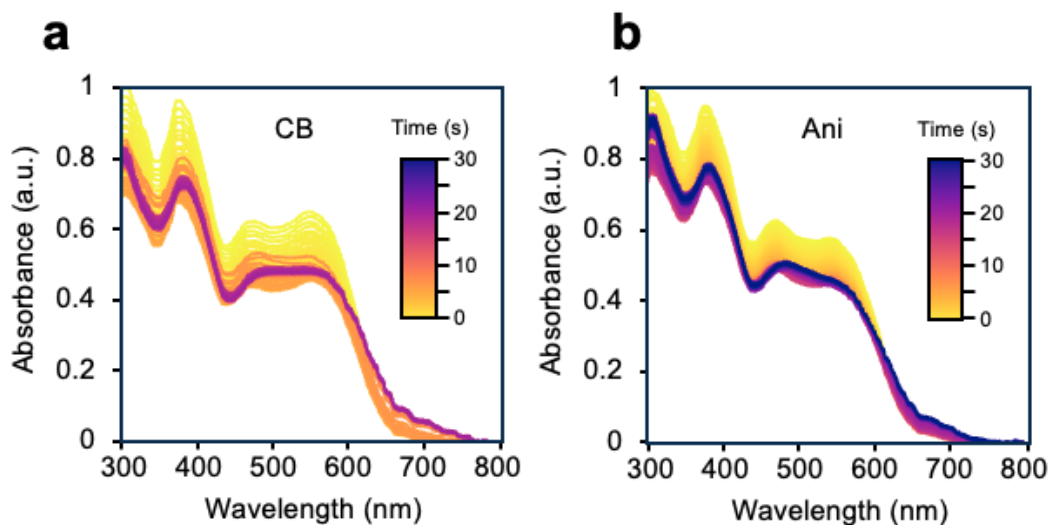


Figure 5.12: (a, b) Time resolved in-situ UV-Vis absorbance profiles of spin-coated films prepared with chlorobenzene 20 mg and anisole 40 mg solutions. (c) Drying times of spin-coated films prepared from three OPV blend solutions: 20 mg in chlorobenzene and 40 mg in anisole.

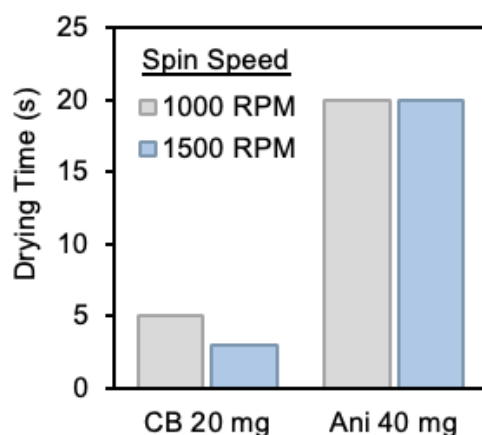


Figure 5.13: Drying times of spin-coated films prepared from three OPV blend solutions: 20 mg in chlorobenzene and 40 mg in anisole.

the two process conditions. The additional annealing step improves device PCE from 4.17% to 4.45%. GIWAXS 2D images show peaks at positions around $q_r = 0.7, 1.3 \text{ \AA}^{-1}$. Although AFM images of spin-coated films do not show significant differences in surface morphology,

increased GIWAXS signal intensity at the $q_r = 1.3 \text{ \AA}^{-1}$ position confirms that the annealing step enhanced the overall crystallinity of the photoabsorbing layer. This suggests that an annealing step can improve device efficiency for devices prepared with the higher boiling point solvent such as anisole.

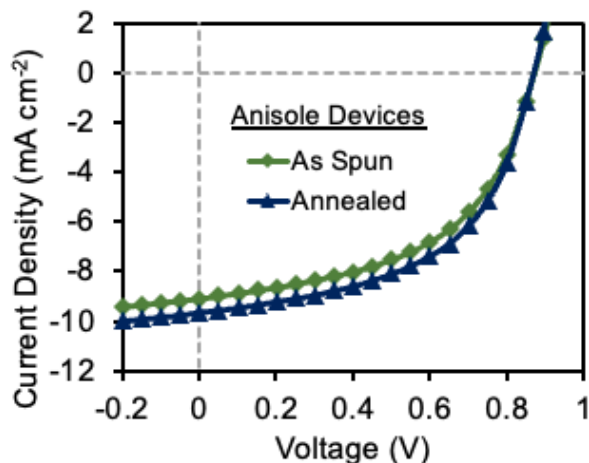


Figure 5.14: (d) Current versus voltage characteristics of OPV devices spin-coated from 40 mg anisole blends. The green line represents devices spun and annealed at room temperature (as-spun) and the blue line represents devices spun and annealed on a hotplate at 70 °C.

Table 5.7: Median and half interquartile ranges of spin-coated anisole OPV devices as-spun and post-annealed at 70 °C.

Solvent	Drying Condition	PCE (%)	FF (%)	Jsc (mA cm ⁻²)	Voc (V)
Anisole	As-spun	4.17 ± 0.04	51.8 ± 0.5	9.4 ± 0.2	0.86 ± 0.01
	Annealed	4.45 ± 0.07	53.4 ± 0.3	9.7 ± 0.1	0.86 ± 0.0

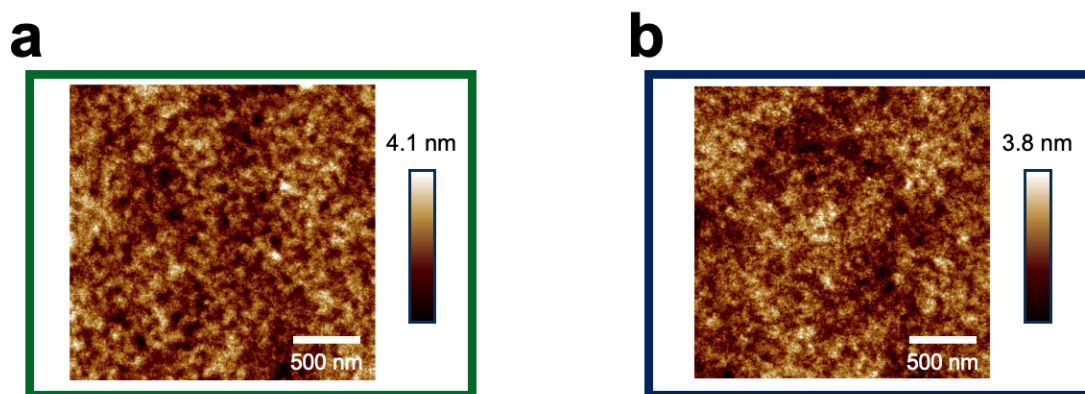


Figure 5.15: 2.5 μm x 2.5 μm AFM images of active films spin-coated from anisole 40 mg solution a) annealed at room temperature with and b) annealed at 70 $^{\circ}\text{C}$ for 10 minutes.

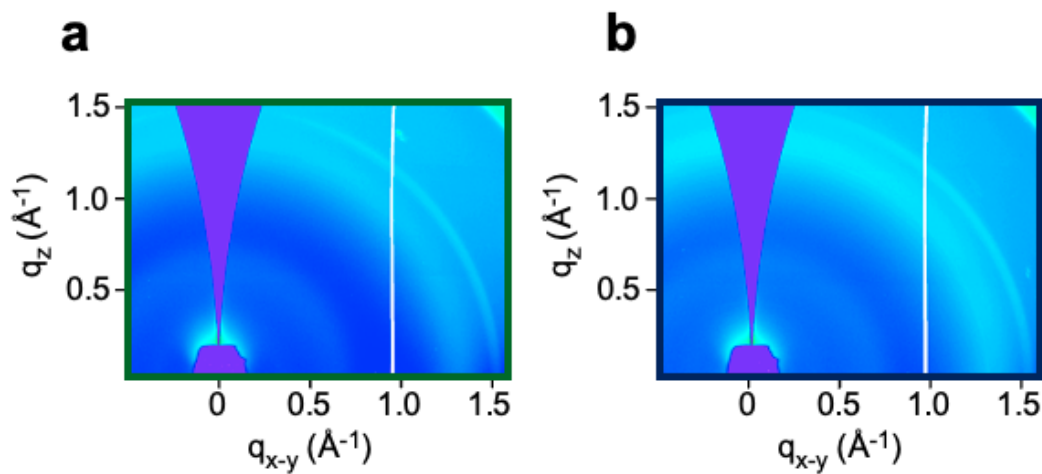


Figure 5.16: GIWAXS 2D images of OPV films as spun and a) annealed at room temperature and b) annealed at 70 $^{\circ}\text{C}$.

5.6 Transition to Printing

Unlike in spin-coating where the air flow generated by the centrifugal force assists in solvent evaporation, in blade-coating the film dries under ambient conditions leading to extended drying times. Additional thermal annealing or airflow is necessary to accelerate solvent drying and reduce prolonged drying and undesired film morphologies. Literature demonstrating green solvent processed OPVs have primarily utilized spin-coating techniques. When blade-coating is demonstrated, many reports favor the addition of hazardous solvent additives to assist in solvent blend evaporation [19, 191–193]. Here, we investigate how processing parameters can influence drying times of films blade-coated from a single greener solvent system.

In-situ UV-Vis measurements were used to investigate the drying times for blade-coated films for 20 mg chlorobenzene and 40 mg anisole solutions. Films were printed at a blade speed and height of 4 cm s^{-1} and 200 microns, respectively. Three processing conditions were investigated: ambient drying, printing on a $70\text{ }^{\circ}\text{C}$ hotplate, and nitrogen airflow used to simulate spin-coating. Example in-situ measurements of printed films are shown in Figure 5.17 for a printed chlorobenzene film.

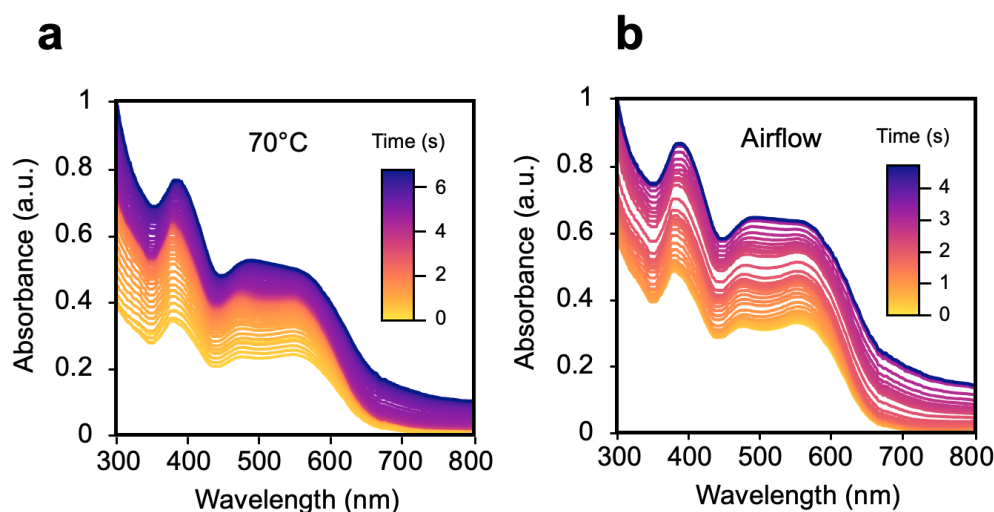


Figure 5.17: Example of time resolved in-situ UV-Vis spectroscopy of printed chlorobenzene films with the different annealing conditions described a) on a $70\text{ }^{\circ}\text{C}$ hotplate and b) nitrogen airflow used to simulate spin-coating.

The summary of drying times extracted are shown in Figure 5.18. The drying times for printed films under ambient conditions were 50 seconds for chlorobenzene and 53 seconds for anisole, roughly 10 times longer than those of spin-coated films. In contrast, films printed on

a hotplate and exposed to airflow dried within 5 to 7 seconds. Unlike in spin-coating where the solvent volatility affects the drying time, in blade-coating, the deposition condition is the primary parameter for determining drying times. Printing on a hotplate or exposing the wet film to nitrogen airflow produced similar drying times to that of the spin-coated chlorobenzene films. Therefore, to achieve comparable device performance, these two drying acceleration techniques were employed.

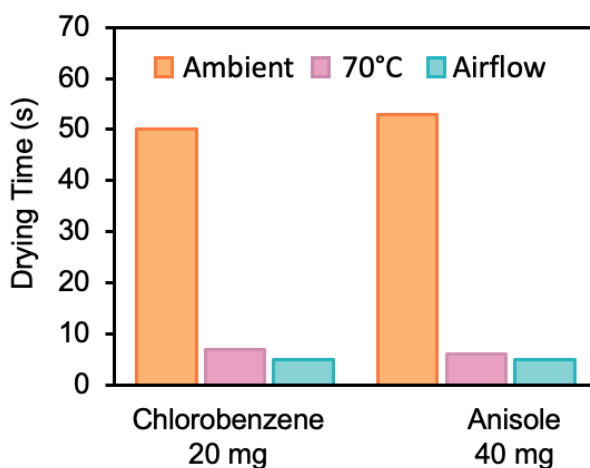


Figure 5.18: Drying times of blade-coated films prepared from two OPV solutions: 20 mg chlorobenzene and 40 mg anisole solution. The films were printed with different conditions: ambient drying, nitrogen airflow, and on a hotplate of 70 °C.

OPVs were blade-coated using the 40 mg anisole solution. The OPVs were either printed on a 70 °C hotplate or exposed to nitrogen airflow. After printing, both conditions were followed by a 10 min annealing step on a 70 °C hotplate. Device characteristics of the printed devices are shown in Figure 5.19 and Table 5.8. Both drying conditions exhibit device efficiencies greater than 4%, similar to spin-coated devices. AFM images of blade-coated films also show similar surface morphologies to previous spin-coated devices as measured with AFM (Figure 5.20). The printed OPVs dried with nitrogen airflow exhibited slightly higher efficiencies and a smaller statistical distribution, suggesting the faster drying time may be advantageous for printed films. Compared to the spin-coated chlorobenzene devices with efficiencies of 4.76%, the printed anisole devices with optimized drying conditions exhibited comparable device efficiencies at 4.22%. With no additional solvent additives, and utilizing a simple conventional device architecture, this is a promising step towards greener solvent processed printed organic solar cells.

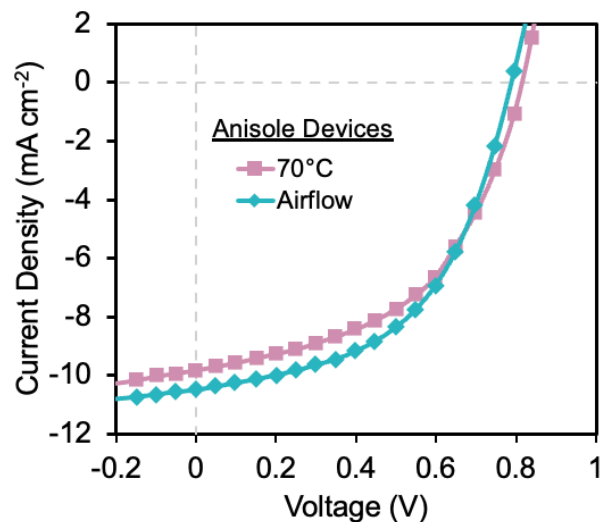


Figure 5.19: Current density-voltage characteristics of printed anisole devices under the two conditions: nitrogen airflow and on a hotplate of 70 °C.

Table 5.8: Median and half interquartile ranges of blade-coated anisole OPV devices exposed to different drying conditions.

Solvent	Drying Condition	PCE (%)	FF (%)	Jsc (mA cm ⁻²)	Voc (V)
Anisole	70 °C	4.05 ± 0.31	48.9 ± 1.4	9.95 ± 0.5	0.82 ± 0.01
	Nitrogen Airflow	4.22 ± 0.13	51.5 ± 1.4	10.58 ± 0.2	0.79 ± 0.01

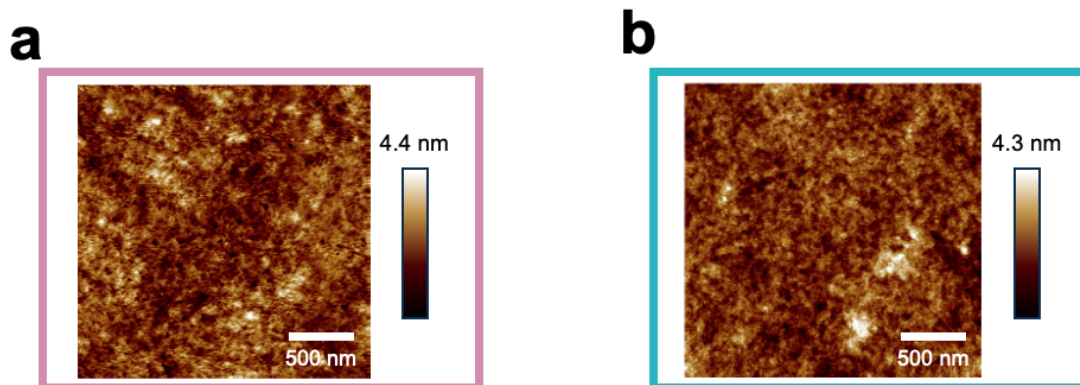


Figure 5.20: 2.5 μm x 2.5 μm AFM images of active films blade-coated with anisole 40 mg solution a) on a at 70 °C hotplate b) dried with nitrogen airflow.

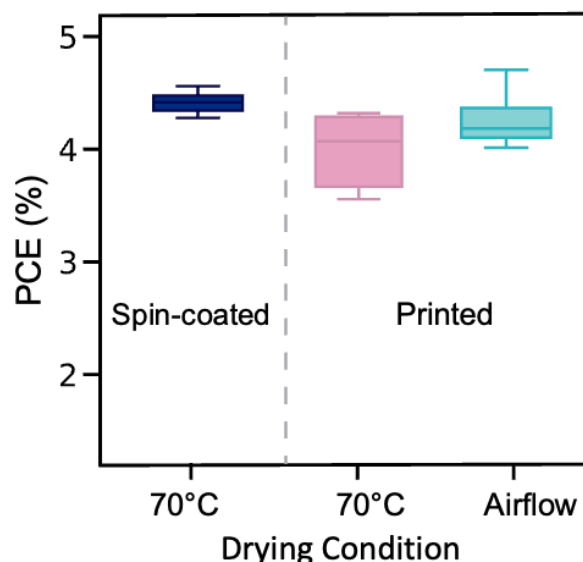


Figure 5.21: Comparison of spin-coated and printed devices fabricated from 40 mg anisole solutions under the two conditions: nitrogen airflow and on a hotplate of 70 °C.

5.7 Conclusion

This work investigated the feasibility of greener solvents in the fabrication of organic solar cells. We utilized a strict and comprehensive selection criterion involving industry-relevant selection guides and investigate greener solvents with larger R_a values typically reported in literature. After initial compatibility tests with different OPV systems and greener solvents, we find that PCDTBT:PC₇₁BM paired with anisole as the greener solvent had the most promising compatibility. Initial results with the greener blend showed that anisole could not simply replace chlorobenzene in solar cell fabrication due to lower semiconductor solubility. Increasing the initial semiconductor mass loaded in anisole increased the resulting solution concentration, better matching the viscosity of the chlorobenzene solution, and more than doubling initial PCEs from 1.68% to 4.17%. Investigating the effect of solvent volatility, we observe that the higher boiling point of anisole increases the spin-coated film's drying time by roughly four times. Employing a post-annealing step after spin-coating helped to enhance crystallinity of anisole devices improving PCE to 4.45%. Finally, the drying times of spin-coated and blade-coated films were compared. Nitrogen airflow during blade coating was shown to significantly reduce the drying time of anisole films, resulting in PCEs of 4.22%. Overall, this work investigated greener processing of OPVs without molecular modifications to the semiconductors and without the use of toxic additives. We demonstrate optimization strategies for the fabrication of solar cells using an industry-relevant greener solvent. This represents an important step towards environmentally friendly and scalable solar cells.

Chapter 6

Conclusions and Future Work

6.1 Summary

This dissertation is a culmination of work focused on steps towards eco-friendly and scalable organic optoelectronic sensors. First, to realize the flexible sensors and validate the practicality of organic electronics in real-world applications, it is essential to develop system architecture that supports the requirements and challenges of these devices. Organic-based PPG sensors, consisting of two different emission OLEDs and a single OPD, were integrated with a custom designed sensor IC. Validating an on-chip reconstruction free sparse-sampling algorithm, the sensor IC demonstrates the ability to reduce power consumption while maintaining high accuracy and reliability of pulse oximetry readings. This work significant advancements in using organic devices in medical applications where power consumption and accuracy of vital sign measurements are critical. Inspired by the multiple devices needed in PPG devices, a novel printing technique for organic electronics is then presented to address the challenges and complexities met during fabrication. A scalable method for printing two devices sided-by-side on a flexible substrate is investigated. The OLEDs and OPDs are printed using a single blade on a single flexible substrate. To ensure high performance for each device, the solution concentration and viscosities are optimized to tune active layer thicknesses. Printed OLEDs were optimized for luminance while OPDs were optimized for responsivities. This is an elegant method for fabricating large-area and low-cost optical sensors where light sources and light detectors are needed, decreasing fabrication complexity and while maintaining device performance. Finally, the environmental impact of large-area fabrication is addressed by analyzing solvent safety and toxicity. Using industry-relevant sources ensures selected solvents are compatible with large-scale manufacturing processes. Hansen solubility theory is discussed as the foundation for selecting greener solvent alternatives compatible for dissolving organic materials. The theory is tested by preparing OPV materials in various greener solvents with increasing Hansen solubility distances and analyzing the concentration of the final solution. Choosing the most compatible donor/acceptor set and greener solvent, methodical optimizations are then presented towards

utilizing an eco-friendly organic solvent in organic solar cell fabrication. In particular, blend formulation, post-processing techniques, and optimization for printing are discussed. This chapter concludes on demonstrating a printed solar device prepared from the optimized greener solvent blend. This work presents the important processing optimizations necessary for fabricating environmentally friendly and scalable organic electronics.

6.2 Suggestions for Future Work

6.2.1 Integrated bandage for wound monitoring

Chapter 2 presented the system developments for organic-based PPG sensors, demonstrating steps towards a compact and conformable wearable pulse oximeter. Oxygenation measurements provided by pulse oximeters are critical for monitoring and assessing conditions of patients with pulmonary diseases such as chronic obstructive pulmonary disease (COPD), asthma, and pneumonia that affect oxygen exchange in the lungs [156, 194, 195]. Another key context in which oxygenation is crucial is in wound healing. Adequate oxygen supply is essential for promoting tissue repair, fighting infection, and supporting cellular processes [196–198]. Conversely, a lack of oxygen in healing wounds can lead to tissue damage and necrosis. Skin wound monitoring can have a significant impact on this public health burden [199]. Using flexible printed sensors with high fidelity sensor-skin interfaces can be implemented as a user-friendly and comfortable wound monitoring device.

Previous work has shown low cost printed flexible electrode arrays used for mapping wounds and electrical stimulation (ES) to promote cell activation for accelerated wound healing [200–202]. Wang and collaborators demonstrated the use of inkjet-printed ES electrodes as a platform for examining molecular mechanisms during the wound healing processes [201]. With this platform, they observed low frequency stimulation (≤ 0.5 Hz) activated inflammatory leukocytes at the wound site. Figure 6.1 shows the fabrication steps of the high density electrode array. The electrodes were prepared on a flexible polyethylene naphthalate (PEN) substrate by inkjet printing a gold electrode array with a gold nanoparticle ink. The finer patterning capability of the inkjet printing process allows for rapid prototyping and fabrication of high-density arrays 6.1b. The electrodes were fabricated on a thin PEN (75 μm) for better flexibility and electrodes were optimized to monitor a 7 mm sized wound. The traces were insulated by attaching a Teflon tape on top, with vias in the tape cut by a laser-cutter. The electrodes were padded with PEDOT:PSS coatings for stable current sourcing, improved charge injection capacity, and improved surface contact. These arrays demonstrated the capability to map areas of varying impedance, as found in wound areas which would have lower impedance in regions with damaged skin compared to undamaged skin. An image of a flexible gold electrode array is shown in Figure 6.1c.

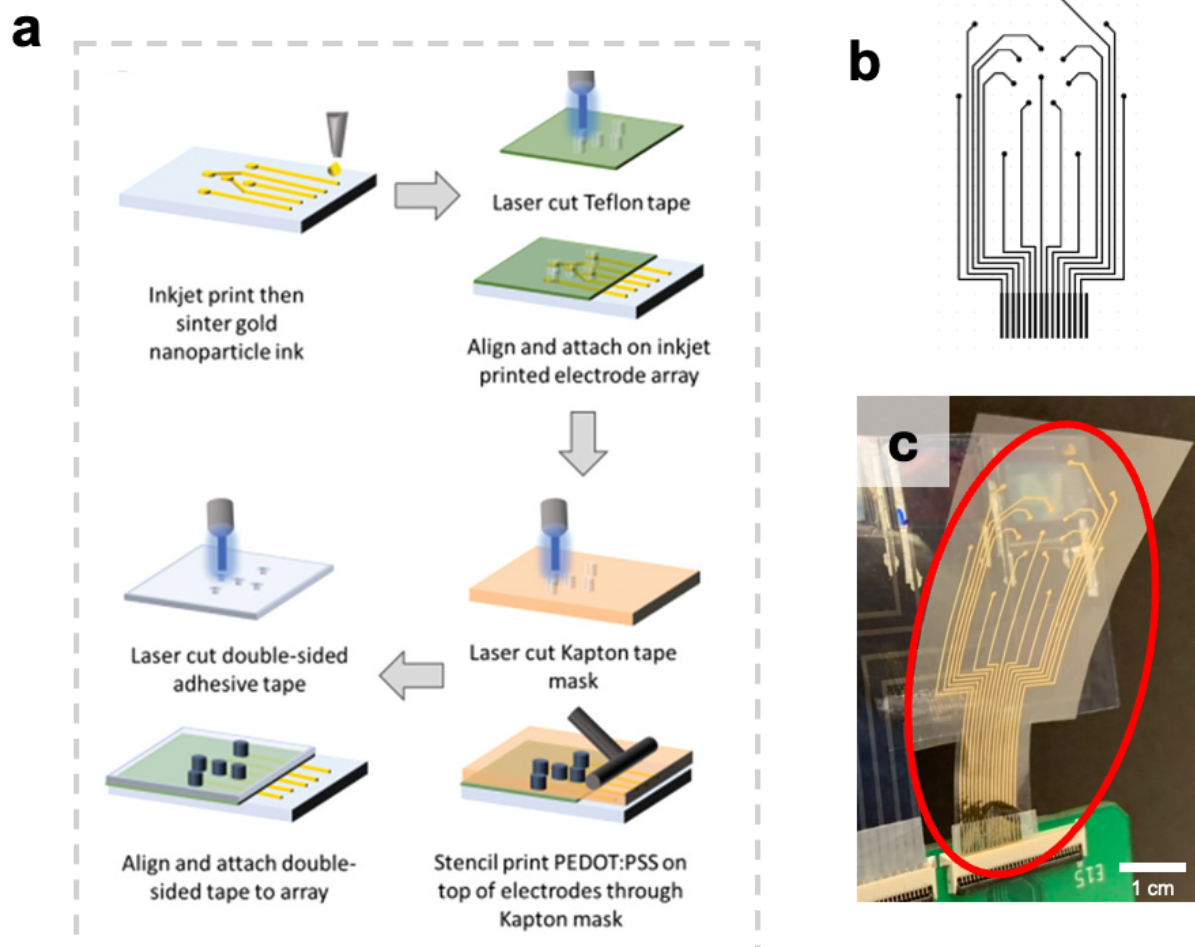


Figure 6.1: a) Fabrication steps of bio-impedance electrodes. Gold electrodes are inkjet printed and sintered on a flexible and transparent PEN substrate. A teflon tape is cut and aligned to the inkjet printed electrode array. Another kapton mask is laser cut to be used as a stencil for applying PEDOT:PSS electrodes on the electrode array. [201] b) Design of the inkjet printed high density electrode array. The distance between the center and inner ring is 2.5 mm, while the distance between the outer ring and inner ring is 5 mm. The electrode diameters are 700 microns. c) Example of a inkjet printed gold electrode array circled in red.

Combining functionalities of a printed electrode array and pulse oximeter would enable an efficient wound monitoring medical device. Utilizing impedance spectroscopy and tissue oxygenation measurements simultaneously would provide a multi-modal approach for comprehensive monitoring of progression of wound healing. The printed electrodes would be used for collecting impedance data while the optoelectronic sensors would be used to perform tissue oxygenation measurements. The fact that electrodes can be printed on transparent plastic substrates facilitates easy integration with optical sensors. Proof of concept the medical device was conducted in collaboration with Professor Juan Zhu and Seiya Ono and shown in Figure 6.2. A single flexible pulse oximeter unit was fabricated with blade-coating techniques on flexible PEN substrates as described in Chapter 3. The pulse oximeter consists of a NIR OLED, a red OLED, and a broad absorption OPD. Aluminum tape and silver paste was used to electrically connect the devices to a transparent carrier substrate with inkjet printed silver traces. The silver traces are then inserted into flat flexible connectors on the custom designed printed circuit board for power and sensor readout. Similarly, the gold bio-impedance electrodes are fabricated via inkjet printing on a flexible and transparent PEN substrate. The printed circuit board consists of an Analog Devices 5933 network analyzer, Texas Instruments AFE4490 analog front end, and a Microchip Technology ATMega 32U4 low-power 8-bit microcontroller designed for controlling and timing the pulse oximetry measurements and periodic impedance spectroscopy measurements. The power is provided by a 9V battery. Figure 6.2e and f show how the integrated sensors can be used for wound monitoring on the arm.

While extensive research exists on flexible sensors, application for wound monitoring and healing remains limited. The described flexible medical sensor, can be fabricated with low-cost printing techniques enabling the potential for disposable bandages. The scalability, cost-effectiveness, and flexibility of these sensors also enable diverse placement on the human body. Future work in integrated printed medical sensors can enable will offer quantitative wound healing measurements that will aid in treatment planning.

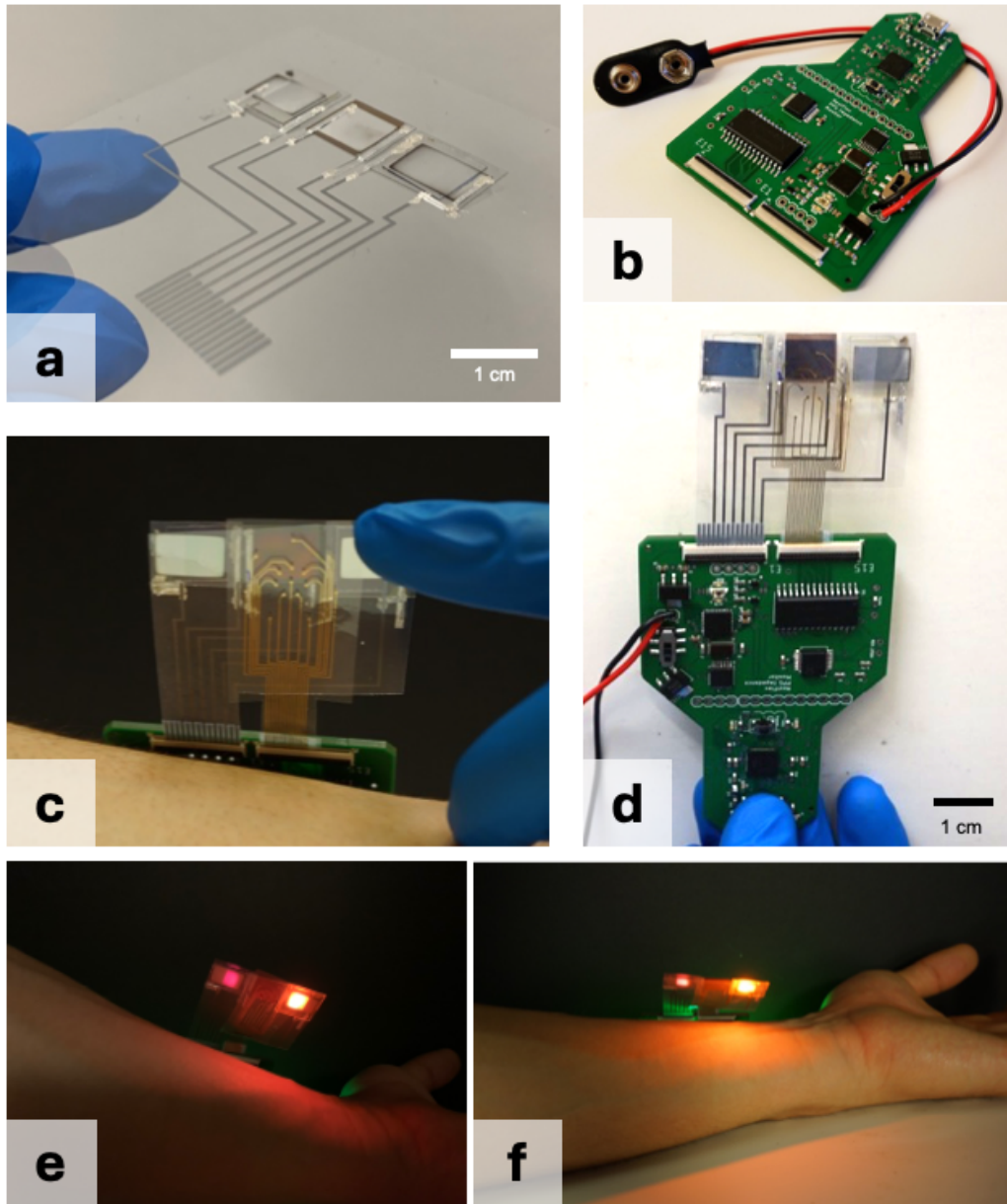


Figure 6.2: a) A single flexible pulse oximeter component consisting of two printed OLEDs and a single OPD at the center. The devices are connected to inkjet printed silver traces. b) Custom designed PCB used to drive OLEDs, take measurements from the photodiode to construct PPG waveforms, and provide periodic monitoring of impedance electrodes. Side-by-side flat flexible connectors are used to connected printed devices. c-d) Image of the devices connected to the printed devices connected to the custom PCB. e-f) Examples of the integrated sensors along a participant's arm demonstrating the use case.

6.2.2 Device Encapsulation

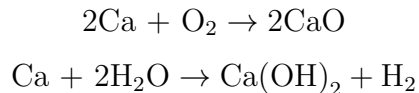
Organic electronics pose many advantages in terms of flexibility, low material waste, and ease of processing compared to their inorganic counterparts. However, organic electronics are often less chemically stable than electronics using inorganic materials in part due to their susceptibility to degradation from water and oxygen [203–205]. Organic materials are inherently prone to oxidation and structural changes. Premature degradation of materials and loss of device integrity are significant barriers to the commercialization of these technologies. For instance, the commercialization of organic solar cells faces significant challenges due to their limited operational lifetime, and is one reason making it difficult to compete in the competitive energy harvesting market [206–208]. In order to extend operational lifetimes and reduce environmental impact of electronic waste, it is crucial to develop durable and reliable electronics.

There are two general approaches for achieving longer device lifetimes: (1) enhancing inherent stability of the materials and structure within the device or (2) encapsulation to increase barriers to the environment and decelerate degradation of the device. First, intrinsic degradation mechanisms pose significant challenges to long-term stability and reliability. These mechanisms can include degradation due to photochemical, thermal, environmental, and operational exposures [208]. To address this, different device structures, materials, and architectures have been proposed and investigated. For instance, one promising approach involves the insertion of the ultrathin protective buffer layers to suppress time-dependent changes at the interfaces between the BHJ and the inorganic charge transporting layers of organic solar cells [209]. Additional UV filter layers can also assist in preventing UV-spectra dependent degradation in active films [210]. However, a drawback of enhancing the inherent stability of materials and devices can be challenging to mitigate entirely. Complex degradation mechanisms may be reduced but at the cost of device performance. On the other hand, encapsulation barriers offer robust physical barriers to environmental factors without which are versatile and can be applied to a range of existing devices without adjustments in device fabrication.

In commercial applications, encapsulation is a critical technology used to enhance the durability, performance, and reliability of many electronics. Organic electronic lifetimes in particular rely on proper permeation barriers from moisture and oxygen to prevent chemical degradation on oxidizable cathodes and functional layers [211]. Commonly, encapsulation of organic devices relies on sequential deposition of thin protective films (Barix, AlOx, parylene, etc.) requiring high-cost deposition processes or sealant materials (UV-curable resins, epoxies) [212, 213]. For instance, commercial OLED displays may employ Al₂O₃/ZrO₂ nanolamination techniques to reduce oxidation, prevent dark spot formation, and ultimately extend efficiency and lifetimes [214]. However, deposition of protective encapsulation layers increase production and material costs of organic electronics. Alternatively, a thin and self-assembly functional nanocomposite developed by Dr. Emma Vargo et al. showed promising

results as a barrier for oxidation and moisture [215].

The nanocomposite barrier presented in their work is simple to deposit, does not require post processing to cure, and shows potential for use as an encapsulant for flexible electronics. As a proof of concept, calcium films were used to investigate their barrier properties. Calcium films rapidly oxidize under ambient conditions and their relative conductance is a convenient proxy for longer-term device degradation. The decreasing conductance of the calcium sample is a result of oxidation in the presence of oxygen and moisture shown in the chemical equations below[216]:



Electrical calcium tests were used to compare the barrier properties of the S2/NP nanocomposite with two standard ultraviolet (UV)-curable epoxies, DELO Katiobond LP655 and Ossila E132. A single sample was prepared on a 125 μm thick PET substrate through a series of thermal evaporation steps. An illustration of the sample is shown in Figure 6.3. A pair of silver traces (100 nm thick, 2 x 15 mm² in size, 4 mm spacing) was thermally evaporated on the PET substrate. Calcium (100 nm thickness, 8 x 8 mm² in area) was thermally evaporated (pressure of 2-5 E⁻⁶ Torr, deposition rate less than 0.8 Å/s) on top of the silver, electrically connecting the two traces. Each sample was then prepared with the designated encapsulant and covered with a 125 μm thick PET cap. For samples testing the nanocomposite barrier, a 20 μL drop of solution was drop-casted, covered with the PET cap, and left to assemble for 1 hour in a nitrogen inert glovebox prior to measurement. Conductance of the encapsulated samples was measured over time in an enclosed environmental chamber maintained at 20% relative humidity and 20 °C.

An image of the encapsulated calcium sample and the associated electrical calcium test results are shown in Figure 6.4. Despite substantial differences in the barrier thickness, their performances are comparable. A 50% relative conductance of the encapsulated calcium films was reached after 241 ± 27 min for DELO Katiobond LP655 (about 119 μm), 367 ± 53 min for Ossila E132 (218 μm encapsulant film thickness) and 79 ± 11 min for S2/NP (about 35 μm). When normalized by the film thickness, the S2/NP barriers nearly double the time until a calcium film reaches 0% relative conductance. Thus, self-assembled nanosheets can lead to thinner and more flexible organic electronics. Furthermore, the transparent barrier ensures compatibility with optoelectronic devices where optical transparency is required.

The collaborative work on self-assembled nanosheets with Dr. Emma Vargo and Professor Ting Xu demonstrate a promising direction for encapsulation of flexible organic devices. At

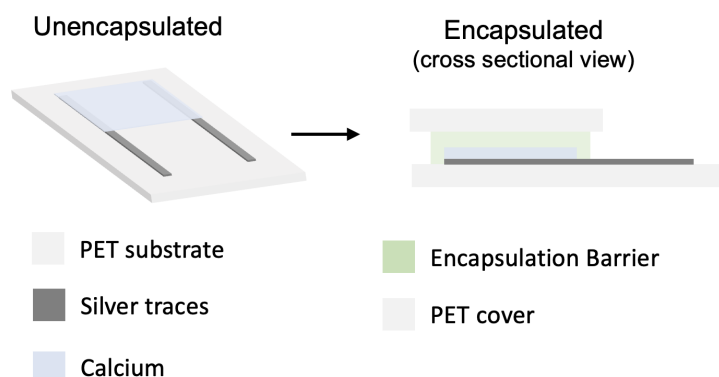


Figure 6.3: Schematic of the encapsulated calcium film tested. The approximate barrier thickness for the commercial encapsulants was calculated based on repeated weight measurements of applied drops and the manufacturer’s reported volumetric densities.

time of writing, chloroform is used to prepare the nanocomposite material. However, because chloroform can dissolve many organic films, it will adversely affect the devices it is applied to. Therefore, to utilize the nanocomposite film as an encapsulation barrier in organic device applications, an orthogonal solvent is needed. Ideally, this solvent should be water- or alcohol-based. Future work should focus on identifying and optimizing such solvents to ensure compatibility and performance in organic electronic devices. Future investigation can also include a focus on thicker barrier films by utilizing printing methods to improve coverage and exploring sequential prints for longer device lifetimes.

6.2.3 Greener Solvent Processing

The solar cell device efficiencies presented in chapter 5 were limited by the solubility of material sets in the chosen green solvent. As a result, PCDTBT and PC₇₁BM was selected as the OPV materials set and further studied in solar cell processing. However, the state of organic solar cell research has developed more efficient materials set. Nonfullerene acceptor (NFA) materials have developed quickly, due to their ease of tunability in absorption spectra and electron energy levels and better complimentary absorption to donor molecules [217]. NFA solar cells have achieved power conversion efficiencies of over 18% as well as high responsivities in organic photodiodes [75, 130, 168, 218, 219]. One material set studied in chapter 5 was PCE10 and IEICO-4F, where PCE10 is a high efficiency polymer donor and IEICO-4F is NFA with absorption in the NIR region. Together, this complimentary donor/acceptor combination was successfully demonstrated in high performance and blade-coated solar cells and photodiodes [52, 220]. When used with the greener solvent anisole, however, PCE10 was shown to have inferior solubility and concentrations not suitable for

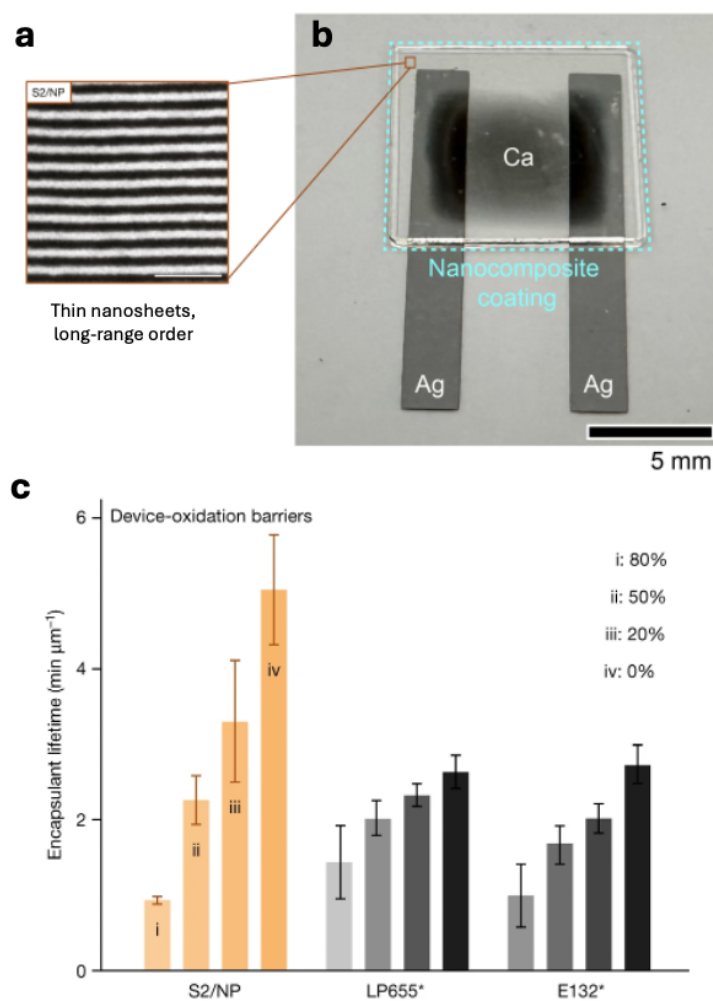


Figure 6.4: a) Cross-sectional TEM image of S2/NP inset (scale bar represents 500 nm). b) Image of encapsulated calcium sample with silver contacts. c) Encapsulant lifetimes of S2/NP and two commercial UV-cured epoxies measured using electrical calcium tests in a 20% relative humidity and 20 °C controlled environment.

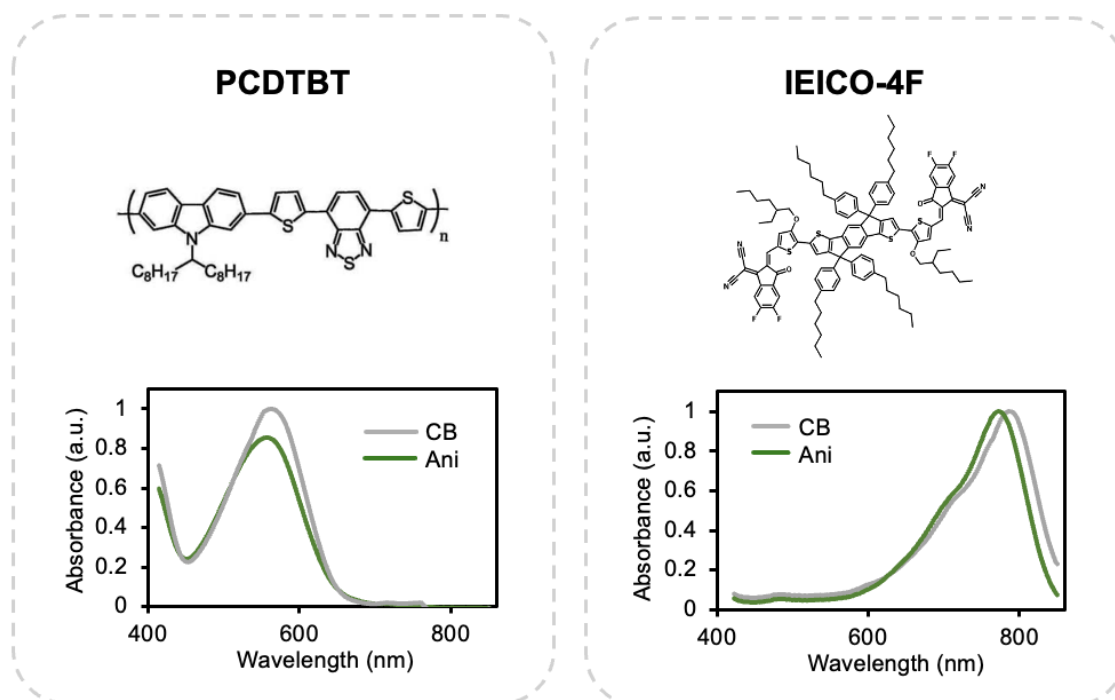


Figure 6.5: Chemical structures and absorption profiles of PCDTBT and IEICO-4F in chlorobenzene and anisole.

film deposition. The polymer donor with the most compatibility with anisole was PCDTBT. On the other hand, IEICO-4F showed a nearly identical concentration in both chlorobenzene and anisole solvents. This can be seen in the absorption profiles of PCDTBT and IEICO-4F solutions in Figure 6.5. Thus, it may be possible to blend together PCDTBT and IEICO-4F for an improved solar cell processed with anisole. Because PCDTBT and IEICO-4F is not commonly combined in OPV solutions, it may require further solution blend optimizations to find an ideal composition and film morphology. Future work should focus on investigating higher efficiency donors and acceptors such as these to increase the PCEs of greener solvent processed solar cells.

Additionally, using a green co-solvent may assist in improving the dissolution of higher molecular weight polymers in non-chlorinated solvents. Recent work in green solvent processing have showed steps towards higher efficiency eco-friendly solar cells, however, incorporation of toxic solvent additives is still commonly used to assist in film deposition, diminishing the impact of utilizing less toxic host solvents [191, 192]. Additional solvents should also be non-toxic and examined under the same manner as the host solvent. For

instance, Corzo et al. demonstrated the use of binary solvent blends using renewable terpene feed-stocks to achieve green solvent processed solar cells with efficiencies up to 15.9 % [62]. They also demonstrate a blade-coated solar cell module of 12 cm² with a power conversion efficiency of up to 9.1%. Future work in greener solvent processing should continue to improve solubility of materials by exploring binary solvent blends and continue to focus on large area printing for scalable and low-cost solar cells.

Appendix A

Appendix

A.1 Chemical Names

Table A.1: Full chemical names of PCDTBT, PC₇1BM, PCE10, IEICO-4F, PM6, and Y6.

Shorthand Name	Full Chemical Name
PCDTBT	Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]
PC71BM	[6,6]-Phenyl-C71-butyric acid methyl ester
PCE10, PTB7-Th, or PBDDTT-EFT	Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2,6-diyl]
IEICO-4F or IOTIC-4F	2,2'-((2Z,2'Z)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile
PM6 or PBDB-T-2F	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
Y6 or BTP-4F	2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile

A.2 Composition Matching Calculations

Variables used in the following calculations are described in the table below:

The donor to acceptor composition ratio can be written:

$$R_{D:A} = \frac{\text{mass}_D}{\text{mass}_A}$$

Table A.2: **Equation Variables**

Variable	Description
mass_D or mass_A	Mass of donor or acceptor in mg
conc_D or conc_A	Concentration of individual donor or acceptor solutions in mg mL^{-1}
vol_D or vol_A	Volume of donor or acceptor in mL
$\text{ratio}_{D:A}$	Donor to acceptor ratio

Volumes of donor and acceptor only solutions depend on the target donor/acceptor ratio and the initial donor-only or acceptor-only solution concentrations. The volume of each individual solution used is determined by the target donor/acceptor ratio.

$$R_{D:A} = \frac{\text{mass}_D}{\text{mass}_A} = \frac{\text{conc}_D \cdot \text{vol}_D}{\text{conc}_A \cdot \text{vol}_A}$$

Thus, given that the target ratio is predetermined, and the donor and acceptor solution concentrations are measured, the volume of either the donor solution or acceptor solution can be calculated based on an arbitrarily chosen volume of its counterpart.

$$\text{vol}_A = \frac{\text{mass}_A}{\text{conc}_A} = \frac{\text{mass}_D}{\text{conc}_A \cdot R_{D:A}} = \frac{\text{conc}_D \cdot \text{vol}_D}{\text{conc}_A \cdot R_{D:A}}$$

$$\text{vol}_D = \frac{\text{mass}_D}{\text{conc}_D} = \frac{\text{mass}_A \cdot R_{D:A}}{\text{conc}_D} = \frac{\text{conc}_A \cdot \text{vol}_A \cdot R_{D:A}}{\text{conc}_D}$$

For instance, for every 1 mL of donor, the amount of $\frac{\text{conc}_D}{\text{conc}_A \cdot R_{D:A}}$ in mL is needed.

The total concentration of this solution can be calculated starting with the following:

$$\text{conc}_{\text{tot}} = \frac{\text{mass}_A + \text{mass}_D}{\text{vol}_A + \text{vol}_D}$$

Here, we want to substitute the variables to only have the target ratio and measured individual donor and acceptor solution concentrations remaining.

Substituting $\text{mass}_A = \text{conc}_A \cdot \text{vol}_A$ and $\text{mass}_D = \text{mass}_A \cdot R_{D:A} = (\text{conc}_A \cdot \text{vol}_A) \cdot R_{D:A}$,

$$\text{conc}_{\text{tot}} = \frac{\text{conc}_A \cdot \text{vol}_A + (\text{conc}_A \cdot \text{vol}_A) \cdot R_{D:A}}{\text{vol}_A + \text{vol}_D}$$

Substituting $\text{vol}_D = \frac{\text{conc}_A \cdot \text{vol}_A \cdot R_{D:A}}{\text{conc}_D}$ from previously,

$$\text{conc}_{\text{tot}} = \frac{\text{conc}_A \cdot \text{vol}_A + (\text{conc}_A \cdot \text{vol}_A) \cdot R_{D:A}}{\text{vol}_A + \frac{\text{conc}_A \cdot \text{vol}_A \cdot R_{D:A}}{\text{conc}_D}}$$

Finally, simplifying by removing vol_A ,

$$\text{conc}_{\text{tot}} = \frac{\text{conc}_A(1 + R_{D:A})}{1 + \left(\frac{\text{conc}_A \cdot R_{D:A}}{\text{conc}_D} \right)}$$

Where conc_A and conc_D are independently measured, and $\text{ratio}_{D:A}$ is the target ratio.

References

- [1] Alison Stowell et al. “Organic electronics: benefits, barriers and opportunities”. In: *Journal of Sustainable Electronics* 8.2 (2020), pp. 123–137.
- [2] Jyoti Bala Kaushal, Pratima Raut, and Sanjay Kumar. “Organic Electronics in Biosensing: A Promising Frontier for Medical and Environmental Applications”. en. In: *Biosensors* 13.11 (Nov. 2023), p. 976. ISSN: 2079-6374. DOI: 10 . 3390 / bios13110976.
- [3] Oksana Ostroverkhova. “Organic Optoelectronic Materials: Mechanisms and Applications”. In: *Chemical Reviews* 116.22 (2016), pp. 13279–13412. ISSN: 15206890. DOI: 10.1021/acs.chemrev.6b00127.
- [4] Tayebbeh Ameri. “Going green at large”. In: *Nature Energy* 6.11 (2021), pp. 1007–1008. ISSN: 20587546. DOI: 10.1038/s41560-021-00936-0.
- [5] Tsuyoshi Sekitani and Takao Someya. “Stretchable, large-area organic electronics”. In: *Advanced Materials* 22.20 (2010), pp. 2228–2246. ISSN: 09359648. DOI: 10.1002/adma.200904054.
- [6] Lulu Sun, Kenjiro Fukuda, and Takao Someya. “Recent progress in solution-processed flexible organic photovoltaics”. en. In: *npj Flexible Electronics* 6.1 (Oct. 2022), pp. 1–14. ISSN: 2397-4621. DOI: 10.1038/s41528-022-00222-3.
- [7] Jonathan Rivnay et al. “Quantitative Determination of Organic Semiconductor Microstructure from the Molecular to Device Scale”. en. In: *Chemical Reviews* 112.10 (Oct. 2012), pp. 5488–5519. ISSN: 0009-2665, 1520-6890. DOI: 10.1021/cr3001109.
- [8] Hong Il Kim et al. “Efficient and Stable Colloidal Quantum Dot Solar Cells with a Green-Solvent Hole-Transport Layer”. en. In: *Advanced Energy Materials* 10.39 (Oct. 2020), p. 2002084. ISSN: 1614-6832, 1614-6840. DOI: 10.1002/aenm.202002084.
- [9] Shitong Li et al. “Recent progress in flexible organic solar cells”. In: *eScience* 3.1 (Feb. 2023), p. 100085. ISSN: 2667-1417. DOI: 10.1016/j.esci.2022.10.010.
- [10] Yinhua Zhou and Chengliang Wang. “Organic optoelectronics creating new opportunities for science and applications”. In: *Frontiers of Optoelectronics* 15.51 (2022). DOI: 10.1007/s12200-022-00052-1.

- [11] Chunhui Liu et al. “Flexible organic solar cells: Materials, large-area fabrication techniques and potential applications”. In: *Nano Energy* 89 (Nov. 2021), p. 106399. ISSN: 2211-2855. DOI: 10.1016/j.nanoen.2021.106399.
- [12] Ana Claudia Arias et al. “Materials and applications for large area electronics: Solution-based approaches”. In: *Chemical Reviews* 110.1 (2010), pp. 3–24. ISSN: 00092665. DOI: 10.1021/cr900150b.
- [13] Saleem Khan, Leandro Lorenzelli, and Ravinder S. Dahiya. “Technologies for printing sensors and electronics over large flexible substrates: A review”. In: *IEEE Sensors Journal* 15.6 (2015). Publisher: IEEE, pp. 3164–3185. ISSN: 1530437X. DOI: 10.1109/JSEN.2014.2375203.
- [14] Noah Strobel et al. “Organic photodiodes: Printing, coating, benchmarks, and applications”. In: *Flexible and Printed Electronics* 4.4 (2019). Publisher: IOP Publishing. ISSN: 20588585. DOI: 10.1088/2058-8585/ab56dd.
- [15] Shiv K. Gupta et al. “Flexible organic semiconductor thin films”. In: *Journal of Materials Chemistry C* 3.33 (2015), pp. 8368–8381. DOI: 10.1039/C5TC00901D.
- [16] Mallory L Hammock et al. “25th anniversary article: The evolution of electronic skin (e-skin): a brief history, design considerations, and recent progress”. In: *Advanced Materials* 25.42 (2013), pp. 5997–6038. DOI: 10.1002/adma.201302240.
- [17] Zhiyuan Zhao et al. “Intrinsically flexible displays: key materials and devices”. In: *National Science Review* 9.6 (2022), nwac090. DOI: 10.1093/nsr/nwac090.
- [18] Ying Diao et al. “Morphology control strategies for solution-processed organic semiconductor thin films”. In: *Energy & Environmental Science* 7.7 (2014), pp. 2145–2159. DOI: 10.1039/C4EE00688G.
- [19] Seungjin Lee et al. “Eco-friendly polymer solar cells: Advances in green-solvent processing and material design”. In: *ACS Nano* 14.11 (2020), pp. 14493–14527. ISSN: 1936086X. DOI: 10.1021/acsnano.0c07488.
- [20] Bradley P. Kirk et al. “Printing and Coating Techniques for Scalable Organic Photovoltaic Fabrication”. en. In: *Materials* 17.11 (May 2024), p. 2511. ISSN: 1996-1944. DOI: 10.3390/ma17112511.
- [21] Qichun Zhang et al. “Recent Progress in Emerging Organic Semiconductors”. en. In: *Advanced Materials* 34.22 (2022), p. 2108701. ISSN: 1521-4095. DOI: 10.1002/adma.202108701.
- [22] Mario Leclerc and Serge Beaupré. “Driving organic electronics to new heights”. en. In: *Nature Materials* 23.5 (May 2024), pp. 589–590. ISSN: 1476-1122, 1476-4660. DOI: 10.1038/s41563-024-01863-7.
- [23] Kolja Kolata et al. “Molecular Packing Determines Singlet Exciton Fission in Organic Semiconductors”. In: *ACS Nano* 8.7 (July 2014), pp. 7377–7383. ISSN: 1936-0851. DOI: 10.1021/nn502544d.

- [24] Veaceslav Coropceanu et al. “Charge Transport in Organic Semiconductors”. In: *Chemical Reviews* 107.4 (2007), pp. 926–952. DOI: 10.1021/cr050140x.
- [25] Wolfgang Brütting and Chihaya Adachi. *Physics of Organic Semiconductors*. en. John Wiley & Sons, Oct. 2012. ISBN: 978-3-527-65496-3.
- [26] Charles Kittel. *Introduction to solid state physics*. en. 8th ed. Hoboken, NJ: Wiley, 2005. ISBN: 978-0-471-41526-8.
- [27] Gabriele Boschetto, Michal Krompiec, and Chris-Kriton Skylaris. “Insights into the Charge-Transfer Mechanism of Organic Photovoltaics: Effect of Domain Size”. In: *The Journal of Physical Chemistry C* 122.30 (Aug. 2018), pp. 17024–17034. ISSN: 1932-7447. DOI: 10.1021/acs.jpcc.8b03409.
- [28] Alberto Salleo et al. “Microstructural characterization and charge transport in thin films of conjugated polymers”. In: *Advanced Materials* 22.34 (2010), pp. 3812–3838. ISSN: 09359648. DOI: 10.1002/adma.200903712.
- [29] Gregory D. Scholes and Garry Rumbles. “Excitons in nanoscale systems”. en. In: *Nature Materials* 5.9 (Sept. 2006), pp. 683–696. ISSN: 1476-4660. DOI: 10.1038/nmat1710.
- [30] Oleksandr V. Mikhnenko, Paul W.M. Blom, and Thuc Quyen Nguyen. “Exciton diffusion in organic semiconductors”. In: *Energy and Environmental Science* 8.7 (2015), pp. 1867–1888. ISSN: 17545706. DOI: 10.1039/c5ee00925a.
- [31] Brian A. Gregg. “Excitonic Solar Cells”. In: *The Journal of Physical Chemistry B* 107.20 (May 2003), pp. 4688–4698. ISSN: 1520-6106. DOI: 10.1021/jp022507x.
- [32] Stephen R. Forrest. *Organic Electronics: Foundations to Applications*. en. Oxford University Press, Aug. 2020. ISBN: 978-0-19-179823-8. DOI: 10.1093/oso/9780198529729.001.0001.
- [33] Osbel Almora et al. “Quantifying the Absorption Onset in the Quantum Efficiency of Emerging Photovoltaic Devices”. In: *Advanced Energy Materials* 11.16 (2021). ISSN: 16146840. DOI: 10.1002/aenm.202100022.
- [34] Y. Shi, J. Liu, and Y. Yang. “Device performance and polymer morphology in polymer light emitting diodes: Morphology dependent emission spectra”. In: *Macromolecular Symposia* 154 (2000), pp. 187–198. ISSN: 10221360. DOI: 10.1002/1521-3900(200004)154:1<187::aid-masy187>3.0.co;2-g.
- [35] Yu Chen et al. “Molecular design toward efficient polymer solar cells processed by green solvents”. en. In: *Polymer Chemistry* 6.22 (2015), pp. 4089–4095. ISSN: 1759-9954, 1759-9962. DOI: 10.1039/C5PY00431D.
- [36] Andrew C. Grimsdale et al. “Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices”. In: *Chemical Reviews* 109.3 (2009), pp. 897–1091. ISSN: 00092665. DOI: 10.1021/cr000013v.

- [37] C. K. Vipin et al. “White Organic Light-Emitting Diodes from Single Emissive Layers: Combining Exciplex Emission with Electromer Emission”. In: *The Journal of Physical Chemistry C* 125.41 (Oct. 2021), pp. 22809–22816. ISSN: 1932-7447. DOI: 10.1021/acs.jpcc.1c06323.
- [38] Juan Chen et al. “Highly efficient near-infrared and semitransparent polymer solar cells based on an ultra-narrow bandgap nonfullerene acceptor”. In: *Journal of Materials Chemistry A* 7.8 (2019). Publisher: Royal Society of Chemistry, pp. 3745–3751. ISSN: 20507496. DOI: 10.1039/c8ta11484f.
- [39] Junshi Liu et al. “Fast Response Organic Tandem Photodetector for Visible and Near-Infrared Digital Optical Communications”. In: *Small* 2101316 (2021), pp. 1–9. ISSN: 16136829. DOI: 10.1002/smll.202101316.
- [40] Takatoshi Tsujimura. *Oled display: fundamentals and applications*. en. 2nd ed. Wiley-SID series in display technology. Hoboken, N. J: Wiley, 2016. ISBN: 978-1-119-18749-3 978-1-119-18732-5.
- [41] Mitsuhiro Kodan. *OLED Displays and Lighting*. en. 1st ed. 2017. ISBN: 978-1-119-04045-3.
- [42] Wolfgang Brütting et al. “Device efficiency of organic light-emitting diodes: Progress by improved light outcoupling”. en. In: *physica status solidi (a)* 210.1 (Jan. 2013), pp. 44–65. ISSN: 1862-6300, 1862-6319. DOI: 10.1002/pssa.201228320.
- [43] Xiaodong Liu et al. “Recent advances in organic near-infrared photodiodes”. In: *Journal of Materials Chemistry C* 6.14 (2018). Publisher: Royal Society of Chemistry, pp. 3499–3513. ISSN: 20507526. DOI: 10.1039/c7tc05042a.
- [44] Boming Xie et al. “Near-infrared organic photoelectric materials for light-harvesting systems: Organic photovoltaics and organic photodiodes”. en. In: *InfoMat* 2.1 (2020), pp. 57–91. ISSN: 2567-3165. DOI: 10.1002/inf2.12063.
- [45] Markus Biele et al. “Spray-Coated Organic Photodetectors and Image Sensors with Silicon-Like Performance”. In: *Advanced Materials Technologies* 4.1 (2019), pp. 1–6. ISSN: 2365709X. DOI: 10.1002/admt.201800158.
- [46] Gerwin H. Gelinck et al. “X-ray imager using solution processed organic transistor arrays and bulk heterojunction photodiodes on thin, flexible plastic substrate”. In: *Organic Electronics* 14.10 (2013). Publisher: Elsevier B.V., pp. 2602–2609. ISSN: 15661199. DOI: 10.1016/j.orgel.2013.06.020.
- [47] Hyunsoo Kim. “Organic Photodiodes and Their Optoelectronic Applications by”. In: (2017).
- [48] Tong Shan et al. “Organic photodiodes: device engineering and applications”. en. In: *Frontiers of Optoelectronics* 15.1 (Dec. 2022), p. 49. ISSN: 2095-2759, 2095-2767. DOI: 10.1007/s12200-022-00049-w.

- [49] Adrien Pierre et al. “High Detectivity All-Printed Organic Photodiodes”. In: *Advanced Materials* 27.41 (2015), pp. 6411–6417. ISSN: 15214095. DOI: 10.1002/adma.201502238.
- [50] Dong Meng et al. “Near-Infrared Materials: The Turning Point of Organic Photovoltaics”. en. In: *Advanced Materials* 34.10 (2022), p. 2107330. ISSN: 1521-4095. DOI: 10.1002/adma.202107330.
- [51] Sri Harish Kumar Paleti et al. “High performance conjugated terpolymers as electron donors in nonfullerene organic solar cells”. In: *Journal of Materials Chemistry C* 8.38 (2020). Publisher: Royal Society of Chemistry, pp. 13422–13429. ISSN: 20507526. DOI: 10.1039/d0tc01379j.
- [52] Xin Song et al. “Controlling Blend Morphology for Ultrahigh Current Density in Nonfullerene Acceptor-Based Organic Solar Cells”. In: *ACS Energy Letters* 3.3 (2018), pp. 669–676. ISSN: 23808195. DOI: 10.1021/acsenergylett.7b01266.
- [53] National Renewable Energy Laboratory (NREL). *Interactive Cell Efficiency Chart*.
- [54] Neeraj Kant and Pushpendra Singh. “Review of next generation photovoltaic solar cell technology and comparative materialistic development”. In: *Materials Today: Proceedings*. First International Conference on Design and Materials 56 (Jan. 2022), pp. 3460–3470. ISSN: 2214-7853. DOI: 10.1016/j.matpr.2021.11.116.
- [55] Mugdha V. Dambhare, Bhavana Butey, and S. V. Moharil. “Solar photovoltaic technology: A review of different types of solar cells and its future trends”. en. In: *Journal of Physics: Conference Series* 1913.1 (May 2021). Publisher: IOP Publishing, p. 012053. ISSN: 1742-6596. DOI: 10.1088/1742-6596/1913/1/012053.
- [56] Martina Schmid. “Revisiting the Definition of Solar Cell Generations”. en. In: *Advanced Optical Materials* 11.20 (2023), p. 2300697. ISSN: 2195-1071. DOI: 10.1002/adom.202300697.
- [57] Justyna Pastuszek and Paweł Wegierek. “Photovoltaic Cell Generations and Current Research Directions for Their Development”. en. In: *Materials* 15.16 (Aug. 2022), p. 5542. ISSN: 1996-1944. DOI: 10.3390/ma15165542.
- [58] Peng Wang et al. “Solution-Processable Perovskite Solar Cells toward Commercialization: Progress and Challenges”. en. In: *Advanced Functional Materials* 29.47 (Nov. 2019), p. 1807661. ISSN: 1616-301X, 1616-3028. DOI: 10.1002/adfm.201807661.
- [59] *Best Research-Cell Efficiency Chart*. en.
- [60] Erik J. Luber and Jillian M. Buriak. “Reporting performance in organic photovoltaic devices”. In: *ACS Nano* 7.6 (2013), pp. 4708–4714. ISSN: 19360851. DOI: 10.1021/nn402883g.

- [61] Chizu Sekine et al. “Recent progress of high performance polymer OLED and OPV materials for organic printed electronics”. In: *Science and Technology of Advanced Materials* 15.3 (2014). Publisher: IOP Publishing ISBN: 1468-6996. ISSN: 14686996. DOI: 10.1088/1468-6996/15/3/034203.
- [62] Daniel Corzo et al. “High-performing organic electronics using terpene green solvents from renewable feedstocks”. In: *Nature Energy* (2022). ISSN: 20587546. DOI: 10.1038/s41560-022-01167-7.
- [63] Julianna Panidi et al. “Biorenewable Solvents for High-Performance Organic Solar Cells”. en. In: *ACS Energy Letters* 8.7 (July 2023), pp. 3038–3047. ISSN: 2380-8195, 2380-8195. DOI: 10.1021/acsenenergylett.3c00891.
- [64] Muhammad Ahsan Saeed et al. “Indoor Organic Photovoltaics: Optimal Cell Design Principles with Synergistic Parasitic Resistance and Optical Modulation Effect”. en. In: *Advanced Energy Materials* 11.27 (2021). eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/aenm.202003103>, p. 2003103. ISSN: 1614-6840. DOI: 10.1002/aenm.202003103.
- [65] Balthazar P. Lechêne et al. “Organic solar cells and fully printed super-capacitors optimized for indoor light energy harvesting”. In: *Nano Energy* 26 (2016), pp. 631–640. ISSN: 22112855. DOI: 10.1016/j.nanoen.2016.06.017.
- [66] Eugen Zimmermann et al. “Erroneous efficiency reports harm organic solar cell research”. In: *Nature Photonics* 8.9 (2014). Publisher: Nature Publishing Group, pp. 669–672. ISSN: 17494893. DOI: 10.1038/nphoton.2014.210.
- [67] Matthew O. Reese et al. “Consensus stability testing protocols for organic photovoltaic materials and devices”. In: *Solar Energy Materials and Solar Cells* 95.5 (2011), pp. 1253–1267. ISSN: 09270248. DOI: 10.1016/j.solmat.2011.01.036.
- [68] Henry J. Snaith. “The perils of solar cell efficiency measurements”. In: *Nature Photonics* 6.6 (2012). Publisher: Nature Publishing Group, pp. 337–340. ISSN: 17494885. DOI: 10.1038/nphoton.2012.119.
- [69] *Effect of parasitic Resistances — PVEducation.*
- [70] Mahmoud N. Zidan et al. “Organic Solar Cells Parameters Extraction and Characterization Techniques”. In: *Polymers* 13.19 (Sept. 2021), p. 3224. ISSN: 2073-4360. DOI: 10.3390/polym13193224.
- [71] M. A. Green. *Solar cells: Operating principles, technology, and system applications*. Jan. 1982. ISBN: 0-85823-580-3.
- [72] Jenny A. Nelson. *The Physics Of Solar Cells*. en. Google-Books-ID: 4Ok7DQAAQBAJ. World Scientific Publishing Company, May 2003. ISBN: 978-1-84816-823-7.
- [73] Yanna Sun et al. “Flexible Organic Solar Cells: Progress and Challenges”. en. In: *Small Science* 1.5 (2021), p. 2100001. ISSN: 2688-4046. DOI: 10.1002/smssc.202100001.

- [74] You Seung Rim et al. “Recent Progress in Materials and Devices toward Printable and Flexible Sensors”. In: *Advanced Materials* 28.22 (2016), pp. 4415–4440. ISSN: 15214095. DOI: 10.1002/adma.201505118.
- [75] Wei Li, Dan Liu, and Tao Wang. “Stability Of Non-Fullerene Electron Acceptors and Their Photovoltaic Devices”. In: *Advanced Functional Materials* 31.41 (2021). ISSN: 16163028. DOI: 10.1002/adfm.202104552.
- [76] Maximilian Moser et al. “Challenges to the Success of Commercial Organic Photovoltaic Products”. en. In: *Advanced Energy Materials* 11.18 (2021). eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/aenm.202100056>, p. 2100056. ISSN: 1614-6840. DOI: 10.1002/aenm.202100056.
- [77] Claire M. Lochner et al. “All-organic optoelectronic sensor for pulse oximetry”. In: *Nature Communications* 5 (2014), pp. 1–12. ISSN: 20411723. DOI: 10.1038/ncomms6745.
- [78] Zhifang Du et al. “High-Performance Wearable Organic Photodetectors by Molecular Design and Green Solvent Processing for Pulse Oximetry and Photoplethysmography”. en. In: *Advanced Materials* 36.9 (2024). eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.202310478>, p. 2310478. ISSN: 1521-4095. DOI: 10.1002/adma.202310478.
- [79] Fahed Elsamnah et al. “Reflectance-Based Organic Pulse Meter Sensor for Wireless Monitoring of Photoplethysmogram Signal”. en. In: *Biosensors* 9.3 (Sept. 2019), p. 87. ISSN: 2079-6374. DOI: 10.3390/bios9030087.
- [80] Juho Kim et al. “Attachable Pulse Sensors Integrated with Inorganic Optoelectronic Devices for Monitoring Heart Rates at Various Body Locations”. In: *ACS Applied Materials & Interfaces* 9.31 (Aug. 2017). Publisher: American Chemical Society, pp. 25700–25705. ISSN: 1944-8244. DOI: 10.1021/acsami.7b05264.
- [81] Hyeonwoo Lee et al. “Toward all-day wearable health monitoring: An ultralow-power, reflective organic pulse oximetry sensing patch”. In: *Science Advances* 4.11 (Nov. 2018). Publisher: American Association for the Advancement of Science, eaas9530. DOI: 10.1126/sciadv.aas9530.
- [82] Hyeonwoo Lee et al. “Organic–Inorganic Hybrid Approach to Pulse Oximetry Sensors with Reliability and Low Power Consumption”. In: *ACS Photonics* 8.12 (Dec. 2021). Publisher: American Chemical Society, pp. 3564–3572. DOI: 10.1021/acsphotonics.1c01161.
- [83] Jeonghyun Kim et al. “Miniaturized Battery-Free Wireless Systems for Wearable Pulse Oximetry”. en. In: *Advanced Functional Materials* 27.1 (2017). eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adfm.201604373>, p. 1604373. ISSN: 1616-3028. DOI: 10.1002/adfm.201604373.

- [84] Haicheng Li et al. “Epidermal Inorganic Optoelectronics for Blood Oxygen Measurement”. en. In: *Advanced Healthcare Materials* 6.9 (2017). _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adhm.201601013>, p. 1601013. ISSN: 2192-2659. DOI: 10.1002/adhm.201601013.
- [85] Yasser Khan et al. “A flexible organic reflectance oximeter array”. In: *Proceedings of the National Academy of Sciences* 115.47 (2018), E11015–E11024. ISSN: 10916490. DOI: 10.1073/pnas.1813053115.
- [86] Tomoyuki Yokota et al. “Ultraflexible organic photonic skin”. In: *Science Advances* 2.4 (Apr. 2016). Publisher: American Association for the Advancement of Science, e1501856. DOI: 10.1126/sciadv.1501856.
- [87] Yana Aleeva and Bruno Pignataro. “Recent advances in upscalable wet methods and ink formulations for printed electronics”. en. In: *Journal of Materials Chemistry C* 2.32 (July 2014). Publisher: The Royal Society of Chemistry, pp. 6436–6453. ISSN: 2050-7534. DOI: 10.1039/C4TC00618F.
- [88] Haveen Ahmed Mustafa Mustafa and Dler Adil Jameel. “Modeling and the main stages of spin coating process: A review”. en. In: *Journal of Applied Science and Technology Trends* 2.02 (Aug. 2021). Number: 02, pp. 119–123. ISSN: 2708-0757. DOI: 10.38094/jastt203109.
- [89] Shuya Wang et al. “Directly Spin Coating a Low-Viscosity Organic Semiconductor Solution onto Hydrophobic Surfaces: Toward High-Performance Solution-Processable Organic Transistors”. en. In: *Advanced Materials Interfaces* 7.8 (2020). _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/admi.201901950>, p. 1901950. ISSN: 2196-7350. DOI: 10.1002/admi.201901950.
- [90] *Spin Coating: Complete Guide to Theory and Techniques*. en.
- [91] Mahmoud Zendejdel et al. “Zero-Waste Scalable Blade-Spin Coating as Universal Approach for Layer-by-Layer Deposition of 3D/2D Perovskite Films in High-Efficiency Perovskite Solar Modules”. en. In: *Solar RRL* 6.3 (2022). _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/solr.202100637>, p. 2100637. ISSN: 2367-198X. DOI: 10.1002/solr.202100637.
- [92] R. Fabian Pease and Stephen Y. Chou. “Lithography and Other Patterning Techniques for Future Electronics”. In: *Proceedings of the IEEE* 96.2 (Feb. 2008). Conference Name: Proceedings of the IEEE, pp. 248–270. ISSN: 1558-2256. DOI: 10.1109/JPROC.2007.911853.
- [93] Rashed Md. Murad Hasan and Xichun Luo. “Promising Lithography Techniques for Next-Generation Logic Devices”. en. In: *Nanomanufacturing and Metrology* 1.2 (June 2018), pp. 67–81. ISSN: 2520-8128. DOI: 10.1007/s41871-018-0016-9.
- [94] Frederik C. Krebs. “Fabrication and processing of polymer solar cells: A review of printing and coating techniques”. In: *Solar Energy Materials and Solar Cells* 93.4 (2009), pp. 394–412. ISSN: 09270248. DOI: 10.1016/j.solmat.2008.10.004.

- [95] J. Z. Wang et al. “Dewetting of conducting polymer inkjet droplets on patterned surfaces”. en. In: *Nature Materials* 3.3 (Mar. 2004). Publisher: Nature Publishing Group, pp. 171–176. ISSN: 1476-4660. DOI: 10.1038/nmat1073.
- [96] Massimiliano Cavallini. “Inhomogeneous thin deposits: a strategy to exploit their functionality”. en. In: *Journal of Materials Chemistry* 19.34 (Aug. 2009). Publisher: The Royal Society of Chemistry, pp. 6085–6092. ISSN: 1364-5501. DOI: 10.1039/B903569A.
- [97] Th Birendra Singh and Niyazi Serdar Sariciftci. “PROGRESS IN PLASTIC ELECTRONICS DEVICES”. en. In: *Annual Review of Materials Research* 36. Volume 36, 2006 (Aug. 2006). Publisher: Annual Reviews, pp. 199–230. ISSN: 1531-7331, 1545-4118. DOI: 10.1146/annurev.matsci.36.022805.094757.
- [98] Sebastiano Cataldo and Bruno Pignataro. “Polymeric Thin Films for Organic Electronics: Properties and Adaptive Structures”. en. In: *Materials* 6.3 (Mar. 2013). Number: 3 Publisher: Multidisciplinary Digital Publishing Institute, pp. 1159–1190. ISSN: 1996-1944. DOI: 10.3390/ma6031159.
- [99] Laxmidhar Nayak et al. “A review on inkjet printing of nanoparticle inks for flexible electronics”. In: *Journal of Materials Chemistry C* 7.29 (2019). Publisher: Royal Society of Chemistry, pp. 8771–8795. ISSN: 20507526. DOI: 10.1039/c9tc01630a.
- [100] Chia Te Yen et al. “Performance Improvement and Characterization of Spray-Coated Organic Photodetectors”. In: *ACS Applied Materials and Interfaces* 10.39 (2018), pp. 33399–33406. ISSN: 19448252. DOI: 10.1021/acsami.8b15140.
- [101] Enrico Sowade et al. “All-inkjet-printed thin-film transistors: manufacturing process reliability by root cause analysis”. en. In: *Scientific Reports* 6.1 (Sept. 2016). Publisher: Nature Publishing Group, p. 33490. ISSN: 2045-2322. DOI: 10.1038/srep33490.
- [102] Jeffrey G. Tait et al. “Determination of solvent systems for blade coating thin film photovoltaics”. In: *Advanced Functional Materials* 25.22 (2015), pp. 3393–3398. ISSN: 16163028. DOI: 10.1002/adfm.201501039.
- [103] Keun Ho Choi, David B. Ahn, and Sang Young Lee. “Current Status and Challenges in Printed Batteries: Toward Form Factor-Free, Monolithic Integrated Power Sources”. In: *ACS Energy Letters* 3.1 (2018), pp. 220–236. ISSN: 23808195. DOI: 10.1021/acsenergylett.7b01086.
- [104] Dennis Cherian et al. “Fabrication of organic photo detectors using inkjet technology and its comparison to conventional deposition processes”. In: *IEEE Sensors Journal* 18.1 (2018). Publisher: IEEE, pp. 94–105. ISSN: 1530437X. DOI: 10.1109/JSEN.2017.2766700.

- [105] T. M. Eggenhuisen et al. “High efficiency, fully inkjet printed organic solar cells with freedom of design”. en. In: *Journal of Materials Chemistry A* 3.14 (Mar. 2015). Publisher: The Royal Society of Chemistry, pp. 7255–7262. ISSN: 2050-7496. DOI: 10.1039/C5TA00540J.
- [106] Adrien Pierre. “Printed Organic Thin Film Transistors, Photodiodes, and Phototransistors for Sensing and Imaging”. English. ISBN: 978-0-355-83133-7 Publication Title: ProQuest Dissertations and Theses 10239980. Ph.D. United States – California: University of California, Berkeley, 2016.
- [107] Adrien Pierre et al. “All-printed flexible organic transistors enabled by surface tension-guided blade coating”. In: *Advanced Materials* 26.32 (2014), pp. 5722–5727. ISSN: 15214095. DOI: 10.1002/adma.201401520.
- [108] Mahsa Sadeghi et al. “Printed Flexible Organic Transistors with Tunable Aspect Ratios”. In: *Advanced Electronic Materials* 6.2 (2020), pp. 1–7. ISSN: 2199160X. DOI: 10.1002/aelms.201901207.
- [109] Donggeon Han et al. “Emission Area Patterning of Organic Light-Emitting Diodes (OLEDs) via Printed Dielectrics”. In: *Advanced Functional Materials* 28.37 (2018). ISSN: 16163028.
- [110] Donggeon Han et al. “Flexible Blade-Coated Multicolor Polymer Light-Emitting Diodes for Optoelectronic Sensors”. In: *Advanced Materials* 29.22 (June 2017). Publisher: Wiley-Blackwell, p. 1606206. ISSN: 15214095. DOI: 10.1002/adma.201606206.
- [111] Juan Zhu et al. “Highly Flexible Transparent Micromesh Electrodes via Blade-Coated Polymer Networks for Organic Light-Emitting Diodes”. In: *ACS Applied Materials and Interfaces* 12.28 (2020), pp. 31687–31695. ISSN: 19448252. DOI: 10.1021/acsami.0c07299.
- [112] Igal Deckman et al. “All-printed full-color pixel organic photodiode array with a single active layer”. In: *Organic Electronics* 56. February (2018). Publisher: Elsevier, pp. 139–145. ISSN: 15661199. DOI: 10.1016/j.orgel.2018.02.009.
- [113] Aminy E. Ostfeld et al. “High-performance flexible energy storage and harvesting system for wearable electronics”. In: *Scientific Reports* 6 (2016). Publisher: Nature Publishing Group. ISSN: 20452322.
- [114] Ricardo E. Sousa, Carlos M. Costa, and Senentxu Lanceros-Méndez. “Advances and Future Challenges in Printed Batteries”. en. In: *ChemSusChem* 8.21 (2015). eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/cssc.201500657>, pp. 3539–3555. ISSN: 1864-564X. DOI: 10.1002/cssc.201500657.
- [115] Anju Toor et al. “Stencil-printed Lithium-ion micro batteries for IoT applications”. In: *Nano Energy* 82 (Apr. 2021), p. 105666. ISSN: 2211-2855. DOI: 10.1016/j.nanoen.2020.105666.

- [116] Andreas Willert et al. “Printing Techniques for Batteries”. en. In: *Printed Batteries*. Section: 2. _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781119287902.ch2>. John Wiley & Sons, Ltd, 2018, pp. 21–62. ISBN: 978-1-119-28790-2. DOI: 10.1002/9781119287902.ch2.
- [117] Dongliang Tian, Yanlin Song, and Lei Jiang. “Patterning of controllable surface wettability for printing techniques”. en. In: *Chemical Society Reviews* 42.12 (May 2013). Publisher: The Royal Society of Chemistry, pp. 5184–5209. ISSN: 1460-4744. DOI: 10.1039/C3CS35501B.
- [118] Martin Kaltenbrunner et al. “Ultrathin and lightweight organic solar cells with high flexibility”. en. In: *Nature Communications* 3.1 (Apr. 2012). Publisher: Nature Publishing Group, p. 770. ISSN: 2041-1723. DOI: 10.1038/ncomms1772.
- [119] Peter Andersson Ersman et al. “All-printed large-scale integrated circuits based on organic electrochemical transistors”. en. In: *Nature Communications* 10.1 (Nov. 2019). Publisher: Nature Publishing Group, p. 5053. ISSN: 2041-1723. DOI: 10.1038/s41467-019-13079-4.
- [120] Elliot J. Strand et al. “Printed Organic Electrochemical Transistors for Detecting Nutrients in Whole Plant Sap”. en. In: *Advanced Electronic Materials* 8.4 (2022). _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/aelm.202100853>, p. 2100853. ISSN: 2199-160X. DOI: 10.1002/aelm.202100853.
- [121] Mark V. Khenkin et al. “Consensus statement for stability assessment and reporting for perovskite photovoltaics based on ISOS procedures”. en. In: *Nature Energy* 5.1 (Jan. 2020), pp. 35–49. ISSN: 2058-7546. DOI: 10.1038/s41560-019-0529-5.
- [122] Gregory C. Welch. “Introduction to Organic Electronics – Ecofriendly and/or sustainable materials, processes, devices, and applications”. en. In: *Journal of Materials Chemistry C* 10.8 (Feb. 2022), pp. 2869–2869. ISSN: 2050-7534. DOI: 10.1039/D2TC90013K.
- [123] Aiman Rahmanudin et al. “Organic Semiconductors Processed from Synthesis-to-Device in Water”. In: *Advanced Science* 7.21 (2020), pp. 1–7. ISSN: 21983844. DOI: 10.1002/advs.202002010.
- [124] Stefan Schlisske et al. “Ink Formulation for Printed Organic Electronics: Investigating Effects of Aggregation on Structure and Rheology of Functional Inks Based on Conjugated Polymers in Mixed Solvents”. In: *Advanced Materials Technologies* 6.2 (2021). ISSN: 2365709X. DOI: 10.1002/admt.202000335.
- [125] Ruijie Ma et al. “Revealing the underlying solvent effect on film morphology in high-efficiency organic solar cells through combined *ex situ* and *in situ* observations”. en. In: *Energy & Environmental Science* 16.5 (2023), pp. 2316–2326. ISSN: 1754-5692, 1754-5706. DOI: 10.1039/D3EE00294B.

- [126] Bright Walker et al. “A systematic approach to solvent selection based on cohesive energy densities in a molecular bulk heterojunction system”. In: *Advanced Energy Materials* 1.2 (2011), pp. 221–229. ISSN: 16146832. DOI: 10.1002/aenm.201000054.
- [127] Samuele Lilliu et al. “Dynamics of crystallization and disorder during annealing of P3HT/PCBM bulk heterojunctions”. In: *Macromolecules* 44.8 (2011), pp. 2725–2734. ISSN: 00249297. DOI: 10.1021/ma102817z.
- [128] Grayson L. Ingram and Zheng-Hong Lu. “Design principles for highly efficient organic light-emitting diodes”. In: *Journal of Photonics for Energy* 4.1 (2014), p. 040993. ISSN: 1947-7988. DOI: 10.1117/1.jpe.4.040993.
- [129] Haiyang Chen et al. “A guest-assisted molecular-organization approach for 17% efficiency organic solar cells using environmentally friendly solvents”. In: *Nature Energy* 6.11 (2021). Publisher: Springer US, pp. 1045–1053. DOI: 10.1038/s41560-021-00923-5.
- [130] Nicola Gasparini et al. “Visible and Near-Infrared Imaging with Nonfullerene-Based Photodetectors”. In: *Advanced Materials Technologies* 3.7 (2018), pp. 1–7. ISSN: 2365709X. DOI: 10.1002/admt.201800104.
- [131] Christian Larsen et al. “A tool for identifying green solvents for printed electronics”. In: *Nature Communications* 12.1 (2021). Publisher: Springer US, pp. 1–7. ISSN: 20411723. DOI: 10.1038/s41467-021-24761-x.
- [132] Pascal Isnard et al. “Sano fi ’ s Solvent Selection Guide: A Step Toward More Sustainable Processes”. In: (2013).
- [133] Fergal P. Byrne et al. “Tools and techniques for solvent selection: green solvent selection guides”. In: *Sustainable Chemical Processes* 4.1 (2016). Publisher: Springer International Publishing, pp. 1–24. ISSN: 2043-7129. DOI: 10.1186/s40508-016-0051-z.
- [134] Denis Prat et al. “CHEM21 selection guide of classical- and less classical-solvents”. In: *Green Chemistry* 18.1 (2015). Publisher: Royal Society of Chemistry, pp. 288–296. ISSN: 14639270. DOI: 10.1039/c5gc01008j.
- [135] Filippo Campana et al. “Green solvent-processed organic electronic devices”. en. In: *Journal of Materials Chemistry C* 8.43 (Nov. 2020). Publisher: The Royal Society of Chemistry, pp. 15027–15047. ISSN: 2050-7534. DOI: 10.1039/D0TC03610B.
- [136] Chunhui Duan et al. “Toward green solvent processable photovoltaic materials for polymer solar cells: the role of highly polar pendant groups in charge carrier transport and photovoltaic behavior”. en. In: *Energy & Environmental Science* 6.10 (Sept. 2013). Publisher: The Royal Society of Chemistry, pp. 3022–3034. ISSN: 1754-5706. DOI: 10.1039/C3EE41838C.
- [137] Shaoqing Zhang et al. “Green-solvent-processable organic solar cells”. In: *Materials Today* 19.9 (2016). Publisher: Elsevier Ltd., pp. 533–543. ISSN: 18734103. DOI: 10.1016/j.mattod.2016.02.019.

- [138] Chunhui Duan et al. “Recent advances in water/alcohol-soluble π -conjugated materials: new materials and growing applications in solar cells”. en. In: *Chemical Society Reviews* 42.23 (Nov. 2013). Publisher: The Royal Society of Chemistry, pp. 9071–9104. ISSN: 1460-4744. DOI: 10.1039/C3CS60200A.
- [139] Junwoo Lee et al. “Green-solvent-processable organic semiconductors and future directions for advanced organic electronics”. en. In: *Journal of Materials Chemistry A* 8.41 (Oct. 2020). Publisher: The Royal Society of Chemistry, pp. 21455–21473. ISSN: 2050-7496. DOI: 10.1039/D0TA07373C.
- [140] Helin Wang et al. “Amino-acid ester derived perylene diimides electron acceptor materials: An efficient strategy for green-solvent-processed organic solar cells”. In: *Dyes and Pigments* 164 (May 2019), pp. 384–389. ISSN: 0143-7208. DOI: 10.1016/j.dyepig.2019.01.047.
- [141] Sergey V. Dayneko, Arthur D. Hendsbee, and Gregory C. Welch. “Fullerene-free polymer solar cells processed from non-halogenated solvents in air with PCE of 4.8%”. en. In: *Chemical Communications* 53.6 (2017), pp. 1164–1167. ISSN: 1359-7345, 1364-548X. DOI: 10.1039/C6CC08939A.
- [142] Yilei Wu et al. “Fine-Tuning Semiconducting Polymer Self-Aggregation and Crystallinity Enables Optimal Morphology and High-Performance Printed All-Polymer Solar Cells”. In: *Journal of the American Chemical Society* 142.1 (Jan. 2020). Publisher: American Chemical Society, pp. 392–406. ISSN: 0002-7863. DOI: 10.1021/jacs.9b10935.
- [143] Charles M. Hansen. *Hansen solubility parameters: A user’s handbook: Second edition*. Publication Title: Hansen Solubility Parameters: A Users Handbook, Second Edition. 2007. ISBN: 978-1-4200-0683-4. DOI: 10.1201/9781420006834.
- [144] Florian MacHui et al. “Determination of solubility parameters for organic semiconductor formulations”. In: *Macromolecular Chemistry and Physics* 212.19 (2011), pp. 2159–2165. ISSN: 10221352. DOI: 10.1002/macp.201100284.
- [145] Jason S. Howell, Benjamin O. Stephens, and David S. Boucher. “Convex solubility parameters for polymers”. en. In: *Journal of Polymer Science Part B: Polymer Physics* 53.16 (Aug. 2015), pp. 1089–1097. ISSN: 0887-6266, 1099-0488. DOI: 10.1002/polb.23753.
- [146] Jason Howell, Miranda Roesing, and David Boucher. “A Functional Approach to Solubility Parameter Computations”. en. In: *The Journal of Physical Chemistry B* 121.16 (Apr. 2017), pp. 4191–4201. ISSN: 1520-6106, 1520-5207. DOI: 10.1021/acs.jpccb.7b01537.
- [147] Natasha A. D. Yamamoto et al. “Charge transport model for photovoltaic devices based on printed polymer: Fullerene nanoparticles”. In: *Solar Energy Materials and Solar Cells* 141 (Oct. 2015), pp. 171–177. ISSN: 0927-0248. DOI: 10.1016/j.solmat.2015.05.034.

- [148] Thue T. Larsen-Olsen et al. “Roll-to-roll processed polymer tandem solar cells partially processed from water”. In: *Solar Energy Materials and Solar Cells*. Dedicated to the Global Organic Photovoltaics (GOPV) conference in Hangzhou, China 97 (Feb. 2012), pp. 43–49. ISSN: 0927-0248. DOI: 10.1016/j.solmat.2011.08.025.
- [149] Thomas R. Andersen et al. “Aqueous Processing of Low-Band-Gap Polymer Solar Cells Using Roll-to-Roll Methods”. In: *ACS Nano* 5.5 (May 2011). Publisher: American Chemical Society, pp. 4188–4196. ISSN: 1936-0851. DOI: 10.1021/nn200933r.
- [150] Ya-Xiong Nan et al. “Generation of native polythiophene/PCBM composite nanoparticles via the combination of ultrasonic micronization of droplets and thermocleaving from aqueous dispersion”. en. In: *Nanotechnology* 22.47 (Nov. 2011), p. 475301. ISSN: 0957-4484. DOI: 10.1088/0957-4484/22/47/475301.
- [151] Yasser Khan et al. “A New Frontier of Printed Electronics: Flexible Hybrid Electronics”. In: *Advanced Materials* 32.15 (2020), pp. 1–29. ISSN: 15214095. DOI: 10.1002/adma.201905279.
- [152] Yasser Muhammad Tasif Khan. “Wearable Medical Sensors Enabled by Printed Bioelectronics and Biophotonics”. English. ISBN: 9798597064628 Publication Title: ProQuest Dissertations and Theses 13422889. Ph.D. United States – California: University of California, Berkeley, 2018.
- [153] Sina Faraji Alamouti. “High-Performance Bio-sensing ICs”. PhD thesis. University of California, Berkeley, 2022.
- [154] Haitao Li et al. “CMOS Electrochemical Instrumentation for Biosensor Microsystems: A Review”. In: *Sensors (Basel, Switzerland)* 17.1 (Dec. 2016), p. 74. ISSN: 1424-8220. DOI: 10.3390/s17010074.
- [155] Jostin Vinroy Dcosta, Daniel Ochoa, and Sébastien Sanaur. “Recent Progress in Flexible and Wearable All Organic Photoplethysmography Sensors for SpO₂ Monitoring”. en. In: *Advanced Science* 10.31 (2023), p. 2302752. ISSN: 2198-3844. DOI: 10.1002/advs.202302752.
- [156] Peter H Charlton et al. “The 2023 wearable photoplethysmography roadmap”. In: *Physiological Measurement* 44.11 (Nov. 2023), p. 111001. ISSN: 0967-3334. DOI: 10.1088/1361-6579/acead2.
- [157] Sina Faraji Alamouti et al. “An SpO₂ Sensor Using Reconstruction-Free Sparse Sampling for 70% System Power Reduction”. en. In: *2022 IEEE International Solid-State Circuits Conference (ISSCC)*. San Francisco, CA, USA: IEEE, Feb. 2022, pp. 344–346. ISBN: 978-1-66542-800-2. DOI: 10.1109/ISSCC42614.2022.9731113.
- [158] Sina Faraji Alamouti et al. “A Sparse Sampling Sensor Front-End IC for Low Power Continuous SpO₂ & HR Monitoring”. en. In: *IEEE Transactions on Biomedical Circuits and Systems* 16.6 (Dec. 2022), pp. 997–1007. ISSN: 1932-4545, 1940-9990. DOI: 10.1109/TBCAS.2022.3223971.

- [159] Hiroaki Jinno et al. “Self-powered ultraflexible photonic skin for continuous bio-signal detection via air-operation-stable polymer light-emitting diodes”. In: *Nature Communications* 12.1 (2021). Publisher: Springer US, pp. 4–12. ISSN: 20411723. DOI: 10.1038/s41467-021-22558-6.
- [160] Donggeon Han et al. “Pulse Oximetry Using Organic Optoelectronics under Ambient Light”. en. In: *Advanced Materials Technologies* 5.5 (2020). eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/admt.201901122>, p. 1901122. ISSN: 2365-709X. DOI: 10.1002/admt.201901122.
- [161] Raleigh L. Davis et al. “Creating controlled thickness gradients in polymer thin films via flowcoating”. In: *Langmuir* 30.19 (2014), pp. 5637–5644. ISSN: 15205827. DOI: 10.1021/la501247x.
- [162] Christopher M. Stafford et al. “Generating thickness gradients of thin polymer films via flow coating”. In: *Review of Scientific Instruments* 77.2 (2006), pp. 1–7. ISSN: 00346748. DOI: 10.1063/1.2173072.
- [163] Jasmine Jan et al. “Flexible Blade-Coated Optoelectronic Devices: Dual Functionality via Simultaneous Deposition”. In: *Advanced Functional Materials* 2112343 (2022), pp. 1–8. ISSN: 16163028. DOI: 10.1002/adfm.202112343.
- [164] Ye Huang et al. “Bulk heterojunction solar cells: Morphology and performance relationships”. In: *Chemical Reviews* 114.14 (2014), pp. 7006–7043. ISSN: 15206890. DOI: 10.1021/cr400353v.
- [165] F. Pelayo García De Arquer et al. “Solution-processed semiconductors for next-generation photodetectors”. In: *Nature Reviews Materials* 2.3 (2017). ISSN: 20588437. DOI: 10.1038/natrevmats.2016.100.
- [166] N. G. Leonard et al. “Organic Photovoltaic New Renaissance: Advances Toward Roll-to-Roll Manufacturing of Non-Fullerene Acceptor Organic Photovoltaics”. In: *Advanced Materials Technologies* 2101556 (2022). ISSN: 2365709X. DOI: 10.1002/admt.202101556.
- [167] Na Gyeong An, Jin Young Kim, and Doojin Vak. “Machine learning-assisted development of organic photovoltaics via high-throughput in situ formulation”. In: *Energy and Environmental Science* 14.6 (2021). Publisher: Royal Society of Chemistry, pp. 3438–3446. ISSN: 17545706. DOI: 10.1039/d1ee00641j.
- [168] Neha Chaturvedi et al. “All Slot-Die Coated Non-Fullerene Organic Solar Cells with PCE 11%”. In: *Advanced Functional Materials* 31.14 (2021), pp. 1–8. ISSN: 16163028. DOI: 10.1002/adfm.202009996.
- [169] Carol L. Baumbauer et al. “Printed, flexible, compact UHF-RFID sensor tags enabled by hybrid electronics”. In: *Scientific Reports* 10.1 (2020). Publisher: Nature Publishing Group UK ISBN: 0123456789, pp. 1–12. ISSN: 20452322. DOI: 10.1038/s41598-020-73471-9.

- [170] C. Amruth et al. “Slot-die coating of double polymer layers for the fabrication of organic light emitting diodes”. In: *Micromachines* 10.1 (2019). ISSN: 2072666X. DOI: 10.3390/mi10010053.
- [171] Mallika Bariya et al. “Roll-to-Roll Gravure Printed Electrochemical Sensors for Wearable and Medical Devices”. In: *ACS Nano* 12.7 (2018), pp. 6978–6987. ISSN: 1936086X. DOI: 10.1021/acsnano.8b02505.
- [172] Dirgha Raj Joshi and Nisha Adhikari. “An Overview on Common Organic Solvents and Their Toxicity”. In: *Journal of Pharmaceutical Research International* 28.3 (2019), pp. 1–18. ISSN: 2454-8405. DOI: 10.9734/jpri/2019/v28i330203.
- [173] Catherine M. Alder et al. “Updating and further expanding GSK’s solvent sustainability guide”. In: *Green Chemistry* 18.13 (2016). Publisher: Royal Society of Chemistry, pp. 3879–3890. ISSN: 14639270. DOI: 10.1039/c6gc00611f.
- [174] Long Ye et al. “Surpassing 10% Efficiency Benchmark for Nonfullerene Organic Solar Cells by Scalable Coating in Air from Single Nonhalogenated Solvent”. In: *Advanced Materials* 30.8 (2018). ISSN: 15214095. DOI: 10.1002/adma.201705485.
- [175] Ying Zhang et al. “Graded bulk-heterojunction enables 17% binary organic solar cells via nonhalogenated open air coating”. In: *Nature Communications* 12.1 (2021). Publisher: Springer US, pp. 1–13. ISSN: 20411723. DOI: 10.1038/s41467-021-25148-8.
- [176] Ling Hong et al. “Eco-Compatible Solvent-Processed Organic Photovoltaic Cells with Over 16% Efficiency”. In: *Advanced Materials* 31.39 (2019). ISSN: 15214095. DOI: 10.1002/adma.201903441.
- [177] Zhifang Du et al. “Insights into Bulk-Heterojunction Organic Solar Cells Processed from Green Solvent”. In: *Solar RRL* 5.8 (2021), pp. 1–11. ISSN: 2367198X. DOI: 10.1002/solr.202100213.
- [178] Changkyun Kim et al. “Green solvent-processed, high-performance organic solar cells achieved by outer side-chain selection of selenophene-incorporated Y-series acceptors”. In: *Journal of Materials Chemistry A* 9.43 (2021). Publisher: Royal Society of Chemistry, pp. 24622–24630. ISSN: 2050-7488. DOI: 10.1039/d1ta07046k.
- [179] Yi-jia Su et al. “Green-Solvent-Processable Organic Photovoltaics with High Performances Enabled by Asymmetric Non-Fullerene Acceptors”. In: (2021). DOI: 10.1021/acsam.1c19627.
- [180] Baobing Fan et al. “Optimisation of processing solvent and molecular weight for the production of green-solvent-processed all-polymer solar cells with a power conversion efficiency over 9%”. In: *Energy and Environmental Science* 10.5 (2017). Publisher: Royal Society of Chemistry, pp. 1243–1251. ISSN: 17545706. DOI: 10.1039/c7ee00619e.

- [181] Wenchao Zhao et al. “Environmentally Friendly Solvent-Processed Organic Solar Cells that are Highly Efficient and Adaptable for the Blade-Coating Method”. In: *Advanced Materials* 30.4 (2018). ISSN: 15214095. DOI: 10.1002/adma.201704837.
- [182] Florian MacHui et al. “Determination of the P3HT:PCBM solubility parameters via a binary solvent gradient method: Impact of solubility on the photovoltaic performance”. In: *Solar Energy Materials and Solar Cells* 100 (2012). Publisher: Elsevier, pp. 138–146. ISSN: 09270248. DOI: 10.1016/j.solmat.2012.01.005.
- [183] Ignasi Burgués-Ceballos et al. “Solubility based identification of green solvents for small molecule organic solar cells”. In: *Advanced Functional Materials* 24.10 (2014), pp. 1449–1457. ISSN: 16163028. DOI: 10.1002/adfm.201301509.
- [184] Luzia P. Novaki et al. “Solvatochromic and Solubility Parameters of Solvents: Equivalence of the Scales and Application to Probe the Solubilization of Asphaltenes”. en. In: *Energy & Fuels* 30.6 (June 2016), pp. 4644–4652. ISSN: 0887-0624, 1520-5029. DOI: 10.1021/acs.energyfuels.6b00461.
- [185] Bin Meng et al. “Replacing Alkyl with Oligo(ethylene glycol) as Side Chains of Conjugated Polymers for Close π - π Stacking”. In: *Macromolecules* 48.13 (July 2015). Publisher: American Chemical Society, pp. 4357–4363. ISSN: 0024-9297. DOI: 10.1021/acs.macromol.5b00702.
- [186] Bin Meng et al. “Phosphonated conjugated polymers for polymer solar cells with a non-halogenated solvent process”. en. In: *Polymer Chemistry* 6.5 (2015), pp. 805–812. ISSN: 1759-9954, 1759-9962. DOI: 10.1039/C4PY01294A.
- [187] Tao Wang et al. “Correlating Structure with Function in Thermally Annealed PCDTBT:PC₇₀ BM Photovoltaic Blends”. en. In: *Advanced Functional Materials* 22.7 (Apr. 2012), pp. 1399–1408. ISSN: 1616-301X, 1616-3028. DOI: 10.1002/adfm.201102510.
- [188] Xinhui Lu et al. “Bilayer order in a polycarbazole-conjugated polymer”. en. In: *Nature Communications* 3.1 (Apr. 2012), p. 795. ISSN: 2041-1723. DOI: 10.1038/ncomms1790.
- [189] Wanjung Kim et al. “Conflicted effects of a solvent additive on PTB7:PC71BM bulk heterojunction solar cells”. In: *Journal of Physical Chemistry C* 119.11 (2015), pp. 5954–5961. ISSN: 19327455. DOI: 10.1021/jp510996w.
- [190] Olesia Synooka et al. “Influence of thermal annealing on PCDTBT:PCBM composition profiles”. In: *Advanced Energy Materials* 4.5 (2014), pp. 2–11. ISSN: 16146840. DOI: 10.1002/aenm.201300981.
- [191] Wenchao Zhao et al. “A universal halogen-free solvent system for highly efficient polymer solar cells”. en. In: *Journal of Materials Chemistry A* 3.24 (June 2015). Publisher: The Royal Society of Chemistry, pp. 12723–12729. ISSN: 2050-7496. DOI: 10.1039/C4TA07029A.

- [192] Christian Sprau et al. “Highly efficient polymer solar cells cast from non-halogenated xylene/anisaldehyde solution”. en. In: *Energy & Environmental Science* 8.9 (Aug. 2015). Publisher: The Royal Society of Chemistry, pp. 2744–2752. ISSN: 1754-5706. DOI: 10.1039/C5EE01917F.
- [193] Ian Pelse et al. “Cosolvent Effects When Blade-Coating a Low-Solubility Conjugated Polymer for Bulk Heterojunction Organic Photovoltaics”. In: *ACS Applied Materials and Interfaces* 12.24 (2020), pp. 27416–27424. ISSN: 19448252. DOI: 10.1021/acsmi.0c04108.
- [194] Shawn P. E. Nishi et al. “Oxygen Therapy Use in Older Adults with Chronic Obstructive Pulmonary Disease”. en. In: *PLOS ONE* 10.3 (Mar. 2015). Publisher: Public Library of Science, e0120684. ISSN: 1932-6203. DOI: 10.1371/journal.pone.0120684.
- [195] Hannah C. Wenger, Adam S. Cifu, and Cathryn T. Lee. “Home Oxygen Therapy for Adults With Chronic Obstructive Pulmonary Disease or Interstitial Lung Disease”. In: *JAMA* 326.17 (Nov. 2021), pp. 1738–1739. ISSN: 0098-7484. DOI: 10.1001/jama.2021.12073.
- [196] Shuning Tian et al. “Hypoxic environment of wounds and photosynthesis-based oxygen therapy”. In: *Burns & Trauma* 12 (Jan. 2024), tkæ012. ISSN: 2321-3876. DOI: 10.1093/burnst/tkæ012.
- [197] F. Gottrup. “Tissue Perfusion and Oxygenation Related to Wound Healing and Resistance to Infection”. en. In: *Immunology and Its Impact on Infections in Surgery*. Ed. by Rainer Engemann, Rene Holzheimer, and A. Thiede. Berlin, Heidelberg: Springer, 1995, pp. 117–126. ISBN: 978-3-642-79079-9. DOI: 10.1007/978-3-642-79079-9_17.
- [198] S. Schreml et al. “Oxygen in acute and chronic wound healing”. eng. In: *The British Journal of Dermatology* 163.2 (Aug. 2010), pp. 257–268. ISSN: 1365-2133. DOI: 10.1111/j.1365-2133.2010.09804.x.
- [199] Chandan K. Sen et al. “Human skin wounds: a major and snowballing threat to public health and the economy”. eng. In: *Wound Repair and Regeneration: Official Publication of the Wound Healing Society [and] the European Tissue Repair Society* 17.6 (2009), pp. 763–771. ISSN: 1524-475X. DOI: 10.1111/j.1524-475X.2009.00543.x.
- [200] Henry C. Lukaski and Micheal Moore. “Bioelectrical impedance assessment of wound healing”. In: *Journal of Diabetes Science and Technology* 6.1 (2012), pp. 209–212. ISSN: 19322968. DOI: 10.1177/193229681200600126.
- [201] Kaiping Wang et al. “A Platform to Study the Effects of Electrical Stimulation on Immune Cell Activation During Wound Healing”. en. In: *Advanced Biosystems* 3.10 (Oct. 2019), p. 1900106. ISSN: 2366-7478, 2366-7478. DOI: 10.1002/adbi.201900106.

- [202] Muhammad Fahad Farooqui and Atif Shamim. “Low Cost Inkjet Printed Smart Bandage for Wireless Monitoring of Chronic Wounds”. en. In: *Scientific Reports* 6.1 (June 2016). Publisher: Nature Publishing Group, p. 28949. ISSN: 2045-2322. DOI: 10.1038/srep28949.
- [203] Franky So and Denis Kondakov. “Degradation mechanisms in small-molecule and polymer organic light-emitting diodes”. In: *Advanced Materials* 22.34 (2010), pp. 3762–3777. ISSN: 09359648. DOI: 10.1002/adma.200902624.
- [204] P. E. Burrows et al. “Reliability and degradation of organic light emitting devices”. In: *Applied Physics Letters* 65.23 (1994), pp. 2922–2924. ISSN: 00036951. DOI: 10.1063/1.112532.
- [205] Ashraf Uddin et al. “Encapsulation of Organic and Perovskite Solar Cells: A Review”. en. In: *Coatings* 9.2 (Feb. 2019). Number: 2 Publisher: Multidisciplinary Digital Publishing Institute, p. 65. ISSN: 2079-6412. DOI: 10.3390/coatings9020065.
- [206] Luke J. Sutherland, Hasitha C. Weerasinghe, and George P. Simon. “A Review on Emerging Barrier Materials and Encapsulation Strategies for Flexible Perovskite and Organic Photovoltaics”. en. In: *Advanced Energy Materials* 11.34 (Sept. 2021), p. 2101383. ISSN: 1614-6832, 1614-6840. DOI: 10.1002/aenm.202101383.
- [207] Qian Lu et al. “A Review on Encapsulation Technology from Organic Light Emitting Diodes to Organic and Perovskite Solar Cells”. en. In: *Advanced Functional Materials* 31.23 (June 2021), p. 2100151. ISSN: 1616-301X, 1616-3028. DOI: 10.1002/adfm.202100151.
- [208] Syed Muhammad Kazim Abbas Naqvi et al. “Unraveling Degradation Processes and Strategies for Enhancing Reliability in Organic Light-Emitting Diodes”. en. In: *Nanomaterials* 13.23 (Jan. 2023). Number: 23 Publisher: Multidisciplinary Digital Publishing Institute, p. 3020. ISSN: 2079-4991. DOI: 10.3390/nano13233020.
- [209] Yongxi Li et al. “Non-fullerene acceptor organic photovoltaics with intrinsic operational lifetimes over 30 years”. en. In: *Nature Communications* 12.1 (Sept. 2021), p. 5419. ISSN: 2041-1723. DOI: 10.1038/s41467-021-25718-w.
- [210] Andrej Classen et al. “Revealing Hidden UV Instabilities in Organic Solar Cells by Correlating Device and Material Stability”. en. In: *Advanced Energy Materials* 9.39 (Oct. 2019), p. 1902124. ISSN: 1614-6832, 1614-6840. DOI: 10.1002/aenm.201902124.
- [211] Sergio Castro-Hermosa et al. “Quantifying Performance of Permeation Barrier—Encapsulation Systems for Flexible and Glass-Based Electronics and Their Application to Perovskite Solar Cells”. en. In: *Advanced Electronic Materials* 5.10 (Oct. 2019), p. 1800978. ISSN: 2199-160X, 2199-160X. DOI: 10.1002/aelm.201800978.

- [212] Ki Suk Kang et al. “Reliable high temperature, high humidity flexible thin film encapsulation using Al₂O₃/MgO nanolaminates for flexible OLEDs”. en. In: *Nano Research* 13.10 (Oct. 2020), pp. 2716–2725. ISSN: 1998-0000. DOI: 10.1007/s12274-020-2915-5.
- [213] Iftikhar Ahmed Channa et al. “Solution processed oxygen and moisture barrier based on glass flakes for encapsulation of organic (opto-) electronic devices”. en. In: *Flexible and Printed Electronics* 6.2 (June 2021), p. 025006. ISSN: 2058-8585. DOI: 10.1088/2058-8585/ac0716.
- [214] Sujith Sudheendran Swayamprabha et al. “Approaches for Long Lifetime Organic Light Emitting Diodes”. In: *Advanced Science* 8.1 (Nov. 2020), p. 2002254. ISSN: 2198-3844. DOI: 10.1002/advs.202002254.
- [215] Emma Vargo et al. “Functional composites by programming entropy-driven nanosheet growth”. en. In: *Nature* 623.7988 (Nov. 2023), pp. 724–731. ISSN: 0028-0836, 1476-4687. DOI: 10.1038/s41586-023-06660-x.
- [216] Eun Ho Song et al. “The flexible Ca-test: An improved performance in a gas permeability measurement system”. en. In: *Review of Scientific Instruments* 82.5 (May 2011), p. 054702. ISSN: 0034-6748, 1089-7623. DOI: 10.1063/1.3584903.
- [217] Jianhui Hou et al. “Organic solar cells based on non-fullerene acceptors”. en. In: *Nature Materials* 17.2 (Feb. 2018). Publisher: Nature Publishing Group, pp. 119–128. ISSN: 1476-4660. DOI: 10.1038/nmat5063.
- [218] Christian B. Nielsen et al. “Non-Fullerene Electron Acceptors for Use in Organic Solar Cells”. In: *Accounts of Chemical Research* 48.11 (Nov. 2015), pp. 2803–2812. ISSN: 0001-4842. DOI: 10.1021/acs.accounts.5b00199.
- [219] Noah Strobel et al. “Non-Fullerene-Based Printed Organic Photodiodes with High Responsivity and Megahertz Detection Speed”. In: *ACS Applied Materials and Interfaces* 10.49 (2018), pp. 42733–42739. ISSN: 19448252. DOI: 10.1021/acsami.8b16018.
- [220] Jasmine Jan et al. “High detectivity, near-infrared organic printed photodiode”. In: *Applied Physics Letters* 124.20 (May 2024), p. 203302. ISSN: 0003-6951. DOI: 10.1063/5.0176156.