Powering the Future: Comprehensive Strategies for Enhancing Efficiency and Stability in Organic Photovoltaic Cells

Andrei Cojocariu

Received October 13, 2023
Accepted April 01, 2024
Electronic access April 15, 2024

Organic photovoltaic (OPV) cells hold great promise for sustainable energy generation, offering a low-cost and eco-friendly alternative to traditional solar cells. However, their efficiency and stability remain key challenges. This paper addresses these challenges through a systematic analysis of three optimization strategies: side-chain modifications, interfacial layer engineering, and morphology optimization. Data tables highlight the impact of these strategies on key OPV cell performance parameters, with the results showing that side-chain modifications improve photon capture and charge transport efficiency, interfacial layer engineering enhances charge collection, and morphology optimization refines material interactions. The integrated application of these strategies offers a promising pathway for advancing OPV cell technology. Through illuminating on the interplay between these strategies and their collective implications, this research contributes to the development of higher efficiency, commercially viable, and long-lasting OPV solar cells.

Introduction

Organic photovoltaic (OPV) solar cells offer a promising alternative to traditional solar cell technologies. Unlike conventional silicon-based solar cells, OPV cells are made from organic materials, typically polymers or small molecules, which offer several key benefits. Firstly, OPV cells can be produced using low-cost and scalable printing techniques, enabling large-scale production at lower costs compared to traditional solar cells1. The inherent flexibility and low density of organic polymers makes the technology highly appealing for applications in flexible and lightweight solar panels, which can be integrated into various surfaces and portable electronics1. OPV cells also offer the potential for tunable and customizable absorption spectra. By designing and synthesizing different organic materials, researchers can tailor the bandgap of OPV materials to capture specific wavelengths of light[1]. OPV cells exhibit excellent low-light performance, allowing them to generate electricity even under overcast or indoor lighting conditions[2–4]. This opens opportunities for designing multi-junction OPV devices that can efficiently harvest solar energy over a broader spectrum of light, leading to improved overall efficiency. Thirdly, OPV cells have a low embodied energy (the sum of all the energy required to produce any goods or services) in their production compared to traditional solar cells[5]. The manufacturing process for organic materials requires less energy and generates fewer greenhouse gas emissions (GHG), making OPV cell technology more environmentally sustainable. The literature on Life Cycle Assessment (LCA) data for solar cells typically focuses on the production stage (cradle-to-gate), often excluding the use and disposal stages[6,7]. This is justified by the disproportionate contribution of the production stage when compared to disposal, with former being 9-10 times higher than the latter[8]. Tsang et al.[9] compared the environmental impact of OPV cells versus conventional technologies using cradle-to-grave LCA data, including disposal. For a rooftop array scenario, assuming landfilling for disposal, they showed that the cumulative CO2-equivalent emissions (CCE) across the life-cycle of a fullerene based OPV cell (OPV-D) was 6.34 kg CO2-eq./m2, compared to 168 CO2-eq./m2 for a traditional silicon-based cell (m-Si).

To take advantage of the OPV cell technology benefits, including flexibility, light weight, lower cost materials or lower GHG emissions during manufacturing, researchers must develop design strategies that address two key limitations of OPV cells, when compared to traditional silicon-based photovoltaic (SPV) cells: cell efficiency and durability. While SPV typically reach efficiencies of 20 – 25%, OPV cells have lower efficiencies, typically 5-10%[10], although higher efficiencies levels of up to 21% have recently been achieved[11,12]. The durability of the OPV cells tends to be lower than SPV due to the organic materials being more susceptible to degradation caused by exposure to the environment, such as moisture, oxygen, heat, and UV radiation[10].

In the context of organic photovoltaic solar cells, the correlation between polymer structure and energy efficiency has garnered significant attention, with a vast body of research exploring this dynamic relationship. Investigations into polymer structure have revealed compelling connections to crucial aspects of solar cell performance. One such correlation lies in the absorption properties of different polymer structures, as they exhibit diverse absorption spectra, enabling targeted light harvesting techniques across specific solar wavelengths. This contributes to improved light absorption and enhanced energy conversion efficiency[10]. Moreover, polymer tunability plays a major role in charge transport and mobility, with well-ordered structures and extended conjugation promoting higher charge carrier mobilities, which facilitates efficient electron and hole extraction[5]. The mobility of these electrons and holes within the polymer layer are directly related to tunable aspects such as the polymer side-chains, conjugation length, and morphology separation within the solar cell. Furthermore, the morphology of the active layer impacts exciton diffusion (the energy absorbed by a particular molecular site is transferred to another nearby molecular site), charge separation, and collection[13].

Researchers have demonstrated that controlling the polymer structure influences phase separation behavior, domain size, and donor-acceptor interpenetration, leading to improved cell efficiency[13]. Additionally, the influence of polymer structure on stability and degradation has been investigated, prompting strategies like molecular weight alteration and donor-acceptor copolymer designs to enhance solar cell durability[14]. In regards to efficiency, side-chain modification and interfacial engineering have emerged as effective approaches to optimize polymer structure and improve charge transport and collection[15,16]. It should be noted that cells stability and cell performance parameters, such power efficiency, are linked to each other. An increase in power efficiency means a larger the amount of light being absorbed and dissipated through non-degradative processes such as charge transport and current generation. This means there are less energy losses, such as heat generation, which tend to have a degradative action on the organic materials in the active layers.

The objective of this review is to explore the impact of polymer structure and morphology on multiple length scales and delve into three key optimizations strategies employed to enhance the efficiency and durability of organic photovoltaic solar cells: side-chain modification, interfacial layer engineering, and morphology optimization.

Methodology

A systematic literature review was conducted to find relevant information on the three OPV cell optimization strategies within the scope of this study. Google Scholar has been used as the main search tool with a time frame of the last decade (2014-2023) and the following keywords: “Organic photovoltaic cells” and “side-chain modification” – 169 results, ”Organic photovoltaic cells” and ”interfacial layer engineering” – 40 results, and ”Organic photovoltaic cells” and ”morphology optimization” and ”polymer blend” – 97 results. The results were further reviewed at title, abstract and references level, selecting studies that performed full cell performance characterization, performed comparative studies across design factors aligned with the 3 optimization strategies, and provided further mechanistic insights. A list of 75 articles was down selected, from which 67 were downloaded in full text, with 46 being used in the final list of references for this review.

The cells examined in this study were evaluated over a range of metrics that are essential for assessing the overall performance, energy conversion capabilities, practicality, and peak power generation potential of the altered OPV cells. Each metric has been thoughtfully selected to provide a comprehensive understanding of the effects of polymer structure on the solar cell’s efficiency and sustainability. Power conversion efficiency (PCE) is a fundamental parameter that quantifies how effectively a solar cell converts incident sunlight into usable electrical energy. By measuring PCE, we gain insights into the inherent efficiency of the altered OPV cells in harnessing solar energy for use. Open-circuit voltage (VOC) signifies the highest voltage that a solar cell can deliver when not connected to an external circuit. It offers critical information about the potential electrical output of the altered OPV cells under no-load conditions. In contrast to this, short-circuit current (JSC) measures the maximum current that a solar cell can deliver when its terminals are directly connected. Understanding this is crucial for assessing the cell’s capacity to generate substantial electrical currents under optimal illumination conditions. Fill factor (FF) quantifies the quality of a solar cell’s electrical output, representing the ratio of the maximum power output to the product of VOC and JSC. This metric offers insights into the efficiency of charge extraction and power delivery, contributing to a holistic understanding of the cell performance.

Results

Functional Mechanism of Organic Photovoltaic Cells

The functional mechanism and working principle of Organic Photovoltaic (OPV) cells is illustrated in Figure 1[17].

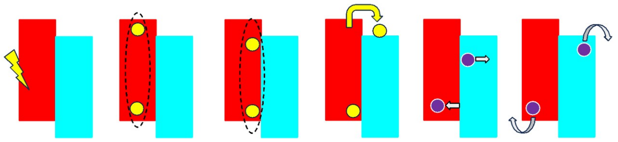

Fig. 1 Figure 1. Functional mechanism of a bilayer organic photovoltaic cell (D = donor, A = acceptor, HOMO – highest occupied orbital, LUMO – lowest unoccupied orbital)[17].

An OPV cell operates by absorbing sunlight through an active layer composed of a blend of polymer donor (D) and acceptor (A) materials. The absorbed photons create excitons, which then diffuse within the polymer blend to reach the donor-acceptor interface[18]. Charge separation occurs at this interface, splitting the excitons into free electrons in the polymer acceptor and positively charged holes in the polymer donor. These charge carriers move through their respective materials, known as charge transport, and are collected at the electrodes as electric current[18]. The generated current flows through an external circuit, producing electricity that can be utilized by a device.

Efficient operation of an OPV cell requires maximizing light absorption and exciton formation, minimizing losses due to exciton recombination (when an electron pairs with a hole and gives up the energy to produce either heat or light), and maximizing charge transport and collection to enhance the overall cell performance. The quest for efficient excitonic solar cells has become a focal point in this domain, with researchers exploring the fundamental relationship between polymer structure and energy efficiency. Research has demonstrated the critical role of polymer design in determining the performance of these cells[19].

Side Chain Modifications

Side-chain engineering offers a viable tool for improving PCE efficiency. Through fine-modification of the alterable side chains of non-fullerene acceptors (NFAs), 17% PCE can be achieved for OPV cells. This is obtained while incorporating a more industrially applicable and scalable method as compared to the more frequently used lab technique of spin-coating[20]. Recent progress in the field of OPV cells has been predominantly driven by the development and adoption of NFAs. These high-performance NFAs exhibit a wide absorption range from 400 to 900 nm, facilitating efficient solar photon capture and generating high output current densities. NFA-based devices demonstrate diminished radiative and non-radiative energy losses, which enables the achievement of elevated voltages for sustained periods of time. This has led to remarkable power conversion efficiencies (PCEs) surpassing 16% in NFA-based OPV cells[20].

Notably, many NFAs are constructed from fused five- or six-membered heterocycles, like ITIC and Y6, which possess extensive conjugated structures promoting ordered intermolecular π–π stacking and enhanced charge transport[20]. However, this characteristic hampers their solubility, posing challenges for solution-based fabrication processes. To address this issue, careful adjustment of the flexible side chains of NFAs is essential to strike a balance between charge transport and solution processability, particularly when scaling up the cell's active area. Presently, large-area OPV cells produced via printing methods achieve a PCE of about 13%, lagging behind smaller-scale spin-coated devices[21]. Most evident is the fact that when employing a blade-coating technique to extend the active layer's dimensions, a notable PCE of 15.5% is sustained, showing evidence of a balanced interplay of solution processability and charge transport[21].

The side-chain alterations studies by Cui et al.[20] and summarized in Table 1, showed that the length of the polymer chain plays a key role in photovoltaic performance among a variety of NFA (non-fullerene acceptors) based cells.

These devices show both reduced radiative and non-radiative energy losses, can obtain high voltages, and are more adept at forming intermolecular $\pi - pi$ stacking to improve charge transport due to their large conjugated structure[22]. The recorded PCE values for cells in which PBDB-TF:BTP-4Cl-8 or PBDB-TF:BTP-4Cl-16 was incorporated into the active layer were lower than those of cells that had an intermediary length with PBDB-TF:BTP-4Cl-12 as the active layer. BTP-4Cl-8 (with 2-ethylhexyl) and BTP-4Cl-16 (with 2-hexyldecyl) cells reached a maximum PCE of 16.3% and 15.6%, respectively[20]. Meanwhile, the more optimal polymer length BTP-4Cl-12 (with 2-butyloctyl) was able to reach 17.0%. Despite having the lowest VOC for the 0.06 cm2 sized cell at 0.858 V, the BTP-4Cl-12 chain had the greatest JSC and FF values of 25.6 mA/cm2 and 0.776 respectively[20]. It is also important to note that these three OPV cells have similar band gaps, E_{loss}s, and molecular energy levels. Ultimately, this demonstrates how polymer chain length can impact current generation and charge extraction efficiencies.

It was also observed that a greater device area impacted measurements in regards to short-circuit current density and fill factor with slight reductions across all cells. However, a more significant change is seen when comparing the different polymer cells when they were manufactured via a spin-coating or blade-coating method. Those whose active layer was constructed with spin-coating experienced greater open-circuit voltage, short-circuit current densities, fill factors, and PCEs. The drop in these parameters from spin-coating to blade-coating production was most notable at the extreme ends of the polymer chain length with the BTP-4Cl-8 and BTP-4Cl-16 cells suffering the greatest losses[20]. The apparent decline in performance can most directly be attributed to decreased charge mobility when the cell was produced via blade-coating. As a result of this, more charge recombination and decreased JSC and FF values greatly impacted the blade-coated cell's efficiency. However, these side-chain modifications still allow for the devices to maintain upwards to 85% of their maximum PCEs even when the active layer thickness is elevated to 300 nm[23]. Furthermore, after 500 hours in the atmosphere these OPV cells were able to maintain 85-90% of their performance capabilities24.

A key practical implication for side chain engineering is that through optimizing the length of the side polymer chains (Cl-12 in Table 1), one can tune the solution processability (i.e. polymer solubility, solution viscosity, film forming ability) to allow scalable manufacturing methods like blade-coating to produce high-area OPV cells with performance similar to lab methods such as spin-coating. Scalable manufacturing methods that can produce devices with high power efficiencies are critical for the development of real-world OPV cell applications. Finding the optimal side chain length must consider the competing phe-

Table 1 Photovoltaic parameters of the OPV cells with side-chain modifications. VOC = Open-Circuit Voltage, JSC = Short-Circuit Current, FF = Fil Factor, PCE = Power Conversion Efficiencies[20].

Active layer	Coating method	VOC (V)	JSC (mA/cm^2)	FF (%)	PCE (%)	Area (cm^2)
PBDB-TF:BTP-4Cl-8	Spin-coating	0.872	25.2	74.3	16.3 (16.1 ± 0.2)	0.06
	Spin-coating	0.863	24.9	71.1	15.3 (14.8 ± 0.3)	0.81
	Blade-coating	0.838	21.7	63.5	11.5 (10.7 ± 0.5)	0.81
PBDB-TF:BTP-4Cl-12	Spin-coating	0.858	25.6	77.6	17.0 (16.6 ± 0.2)	0.06
	Spin-coating	0.853	25.4	77.2	16.7	0.06
	Spin-coating	0.849	25.5	73.8	16.0 (15.5 ± 0.3)	0.81
	Blade-coating	0.833	26	71.6	15.5 (14.9 ± 0.4)	0.81
PBDB-TF:BTP-4Cl-16	Spin-coating	0.862	24.2	74.8	15.6 (15.2 ± 0.2)	0.06
	Spin-coating	0.854	24	71.8	14.7 (14.2 ± 0.3)	0.81
	Blade-coating	0.807	19.4	68.9	10.8 (9.81 ± 0.6)	0.81

nomena of increasing the solubility of conjugated polymers, favored by long alkyl chains that enable solvent penetration, and increasing the charge transporting performance in semiconducting polymers, which is favored by short alkyl chains that have minimal interference with molecular stacking and crystalinity[24].

Interfacial Layer Engineering

Interfacial engineering offers another viable route for increasing performance in organic photovoltaic cells. Many published studies[25–27] advocate for the applications of organic materials as interfacial layers (IFLs). The authors discuss the importance of interfacial engineering in achieving high power conversion efficiencies (PCEs) in OPV cells and highlight the underlying device physics and the origins of enhanced PCEs by IFLs. As shown in Figure 2 (a), these IFLs are sandwiched between the BHJ (Bulk heterojunction) composite and the electrodes and modify the interface to improve charge carrier transport properties[25].

Different types of IFLs have been investigated, including PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate), metals, salts, metal oxides, and water/alcohol soluble organic materials[25]. The role and significance of each type of interfacial layer (IFL) are discussed, along with their impact on enhancing PCEs . These materials offer tunable electrical properties through structural modification and can be deposited on top of or underneath the BHJ composite without damage. The enhanced PCEs are attributed to the formation of dipole moments at the BHJ composite/electrode interface, doping effects, and improved surface electrical conductivities[25].

The literature also discusses the formation of ohmic contact between the organic materials and the electrodes[25]. An ohmic contact is a junction between two conductors that has a linear current–voltage and exhibits low resistance over a wide range of applied voltages. This is crucial for efficient charge carrier transport and reduced recombination . The introduction of IFLs helps adjust the energy barriers and improve charge carrier selectivity (Figure 2-b), leading to enhanced PCEs in the cells. Improved charge carrier selectivity is critical for the power efficiency of a solar cells as it ensures that the two charge carriers (electrons and holes) are efficiently collected at the two corresponding electrodes (cathode and anode) to generate an electric current. Poor charge carrier selectivity results in recombination of the two charges before being collected by the corresponding electrodes, emitting light or heat instead of generating a current, and therefore resulting in poor power efficiency.

As depicted in Figure 2, the BHJ composite is positioned between an indium tin oxide (ITO) electrode and a metal electrode, forming an ITO/BHJ composite/metal sandwich structure[25]. The electron donor (D) and electron acceptor (A) components within the BHJ composite are closely connected to the electrodes, leading to the separation of electrons and holes, which tend to recombine at the BHJ composite/electrode interfaces[27]. Energy barriers arise from the mismatch between electrode work functions, an important parameter that dictates energetic landscape at the interfaces and the density of charges formed upon the contact[28], and D or A energy levels, impeding efficient charge carrier collection. To address these challenges, IFLs, known as electron extraction layers (EELs) or hole extraction layers (HELs), are introduced to modify the BHJ composite/electrode interfaces[27]. EELs and HELs create low-resistance contact points, reducing energy barriers and enhancing charge carrier selectivity at these interfaces, thus curbing charge recombination[27]. This integration of IFLs significantly improves power conversion efficiencies (PCEs) of OPV cells. Furthermore, the insertion of IFLs enables the adjustment of OPV cell polarity, facilitating the use of high work function metals like silver (Ag) or gold (Au) as anodes. They are also key from the viewpoint of sustainability as IFLs are known to be able to prevent oxygen and moisture penetration in the BHJ composite and electrode interface, increasing cell stability and prolonging the performance lifetime of these cells.

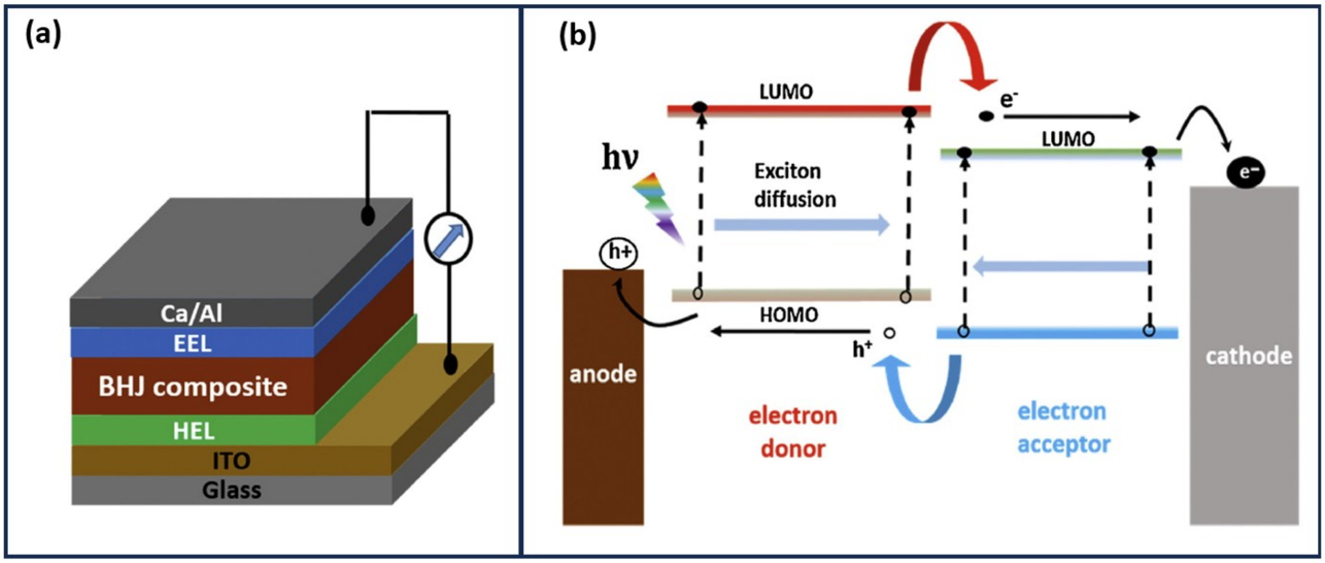

Fig. 2 Figure 2. (a) Device structures of OPV cells, where $Ca/Al = Calcium/Aluminum$, $EEL = electronextractionlayers$, $BHJ = bulkheterojunction$, $HEL = holeextractionlayers$, $ITO = IndiumTinOxide$. (b) Working principles of OPV cells, where LUMO = lowest unoccupied molecular orbital, HOMO = highest occupied molecular orbital, $h+ = hole$, $e- = electron$, $hv = photon$[25].

One prominent polymer example used as an IFL is PEDOT:PSS. It is a doped polymer and one of the earliest interfacial layers (IFLs) used in OPV cell development. Utilized in a cell, it can establish an ohmic contact between the BHJ composite and the ITO electrode, facilitating hole transport rather than electron transport. The presence of PEDOT:PSS thin film on the ITO electrode surface leads to smoother surfaces, reducing leakage current and aiding in the transport of holes. Additionally, its solution processability, transparency in the visible spectrum, and high electrical conductivity make it a popular choice in OPV cells[26]. One drawback, however, is the acidic nature of PEDOT:PSS that can etch the ITO surface and negatively impact cell lifetime[29,30]. Water/alcohol soluble organic materials such as conjugated polymers, fullerene derivatives, and graphene oxide offer creative solutions to this challenge via tunable structures and hence properties[25]. However, fullerene derivatives also have some limitations including weak absorption in the abundant region of the incident solar spectrum and limited tunability in terms of spectral absorption[31]. Some of these limitations are being addressed by the research community through developing new non-fullerene acceptors (NFA), such as thiophenes-based structures having a broad absorption spectrum from 400 to 900 enabling PCE of up to 17%[20,32].

Chao et al. has studied the effect of different interfacial engineering materials for high performance OPV cells[25]. Figure 3, shows examples of molecular structures used as materials for IFL engineering including conjugated polymers, non-conjugated polyelectrolytes, fullerene derivatives, graphene oxide and small molecules[25] .

The two primary materials considered in this IFL alteration were conjugated polymers and fullerene derivatives. When looking at the impacts of incorporating conjugated polymers such as PEDOT:PSS into IFLs, an increase in overall cell performance is observed . The thin IFL film smooths the surface of the ITO and mitigates leakage current, which consequently helps with the transportation of holes through the cell[25]. The majority of the reported data placed these OPV cells in the 6.2-6.9% PCE range, which is a significant improvement from the OPV cells where commonly used perylene diimide (PDI) based cells reported values anywhere from 0.57 to 3.45% PCE[5]. Without significant leaps in regards to measured open-circuit voltage, the greatest contributor to a larger FF and PCE in these conjugated polymer IFL cells was from the increase in short-circuit current density (see Table 2).

Short-circuit current density (JSC) in these cells ranged from 9.89-16.76 mA/cm2[25]. Charge carrier collection efficiency greatly improves with IFLs as EELs or HELs are implemented to optimize the BHJ composite/electrode interface and reduce existing energy barriers that limit transport through the cell[27]. Fullerene derivatives also aim to achieve the same results as conjugated polymer IFLs. According to Table 2, these fullerene-based cells tend to have more consistent open circuit voltage measurements that gravitate around ∼0.88 V[25]. Similarly, their JSC and FF values are more consistent as compared to conjugated polymers that can produce a wide range of results and graphs at both ends of the spectrum. This is likely do to the larger structural differences, for both BHJ composites and IFLs, among the conjugated polymers samples versus the fullerene

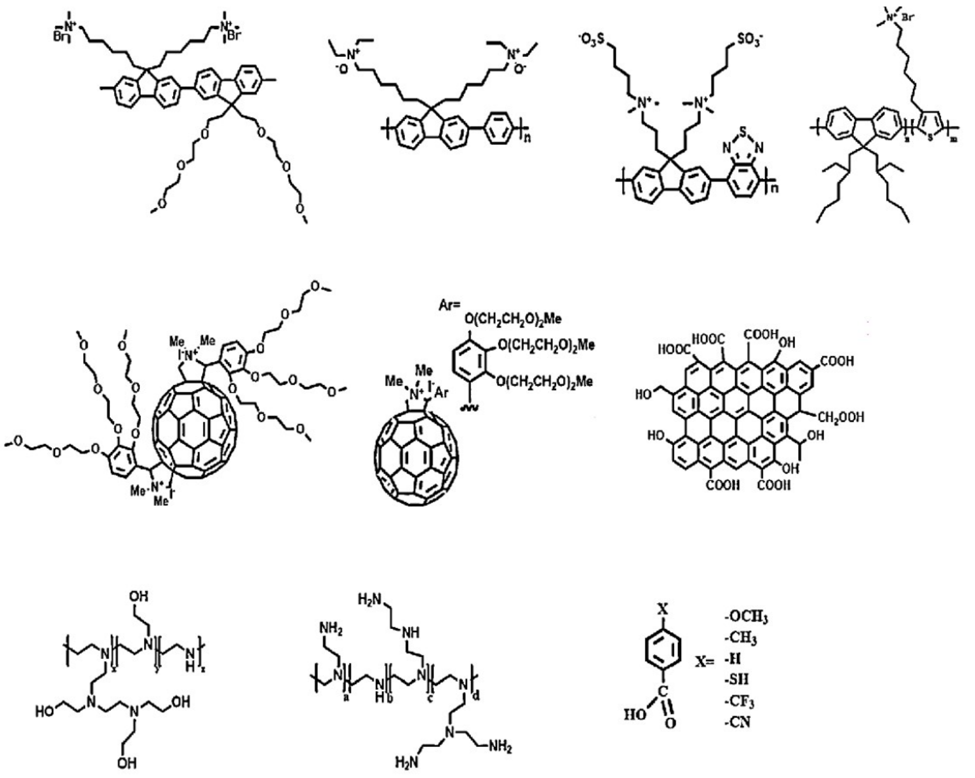

Fig. 3 Molecular structures of organic materials used as the interfacial layers in OPV cells, including conjugated polymers (WPF-6-oxy-F, PF6NO25-py, PFNSO-BT, PF2/6-b-P3MAHT), fullerene derivatives (Bis-PC61BM, ETL-1), graphene oxide, non-conjugated electrolytes (PEI, PEIE) and small molecules (substituted benzoic acids)[25].

Table 2 IFL materials, device structures and OPV cell performance parameters of cells with IFLs. VOC = Open-Circuit Voltage, JSC = Short-Circuit Current, FF = Fil Factor, PCE = Power Conversion Efficiencies[25].

Type of materials	Materials	Device structures	VOC (V)	JSC (mA/cm^2)	FF (%)	PCE (%)
Conjugated polymers	WPF-6-oxy-F	ITO/PEDOT:PSS/P3HT:PC61BM/IFL/Al	0.62	9.89	59	3.67
	PF6NO25-py	ITO/PEDOT:PSS/PCDTBT:PC71BM/IFL/Al	0.91	11.6	66.2	6.9
	PFNSO-BT	ITO/PEDOT:PSS/PTB7:PC71BM/IFL/Al	0.65	16.76	61.1	6.61
	PF2/6-b-P3TMAHT	ITO/PEDOT:PSS/PCDTBT:PC71BM/IFL/Al	0.89	10.6	67	6.2
Fullerene derivatives	bis-PC61BM	ITO/PEDOT:PSS/PIDT-PhanQ:PC71BM/IFL/Al	0.88	11.19	60	5.87
	bis-PC61BM	ITO/PEDOT:PSS/PIDT-PhanQ:PC71BM/IFL/Ag	0.88	11.5	61	6.22
	ETL-1	ITO/PEDOT:PSS/PIDT-PhanQ:PC71BM/IFL/Ag	0.87	11.28	64	6.28
	ETL-1	ITO/PEDOT:PSS/PIDT-PhanQ:PC71BM/IFL/Al	0.86	11.17	62	5.96

derivative samples presented in Table 2. While for the fullerene derivative samples, the device structure was varied only around the IFLs, the device structure for the conjugated polymers was also varied around the donor material in the BHJ composite. Also, analyzing Figure 3, the structural differences among the fullerene derivatives samples are smaller (only the substituents to the fullerene buckyball are varied) when compared to the structural difference among the conjugated polymers samples (both the substituents and the conjugated structure are varied). Due to their slightly lower short-circuit current densities of around 11.2 mA/cm2, cells that use fullerene derivatives for IFLs achieve slightly lower PCE recordings of around 5.87%-6.28%[33].

Overall, IFLs offer charge carrier selectivity, which reduces the likelihood of charge recombination at the BHJ composite/electrode interfaces, and reduce the energy barriers for charge transport between the BHJ composite and the electrodes to enable higher power efficiency. It has been suggested that the increase in PCE and specifically VOC values for IFL cells is a result of the formation of dipole moments and ohmic contact at the interface, although the effect a potential doping effect could not be ruled out due to the very thin films used in the study[25]. The improvements provided by IFL engineering can result in major industrial gains considering how advantageous the low cost, flexible, clean, and high throughput nature of BHJ manufacturing is. As a result, incorporating different configurations in OPV cells that take advantage of IFLs is worth consideration[26].

Morphology Optimization

Another key modification technique used to enhance the PCE of many OPV cells involves morphology control. The optimization of all-polymer solar cells involves many factors such as phase separation, interpenetrating network structure, molecular stacking, and polymer chain orientation[34]. Effective interfaces between polymer donors and acceptors are proposed to mitigate recombination and enhance efficiency. In All-PSCs, the active layer's phase-separated domain structures tend to be larger due to polymer chain entanglement and low mixing entropy, distinguishing them from fullerene-based and small molecules-based PSCs[35]. Charge transfer efficiency in All-PSCs relies on molecular stacking and polymer chain orientation, where face-on orientation enhances charge separation and transport[36]. The molecular stacking is very important because it provides the necessary spatial overlapping and orientation of the molecular orbitals involved in Donor/Acceptor charge transfer, which produces the charge separation, as well as in charge delocalization through conjugation, which is responsible for charge transport to the corresponding electrodes[17]. When the conjugated polymers adopt a face-on orientation in relationship to the substrate, charge mobility is improved due to the increased ability of the holes to travel through a stacked -conjugation network[37]. However, due to surface energetics, many semiconducting polymers favor chain conformations where their side chains are perpendicular to the layer surface, resulting in an edge-on orientation of the polymer backbone, where the holes must hop between polymer chains for charge transport and collection[38]. Therefore, special considerations must be taken to achieve morphologies that maintain a face-on orientation in PSCs. For example, processing techniques such as solvent additives or sequential processing (SqP, where the polymer film is deposited first, and then the fullerene is infiltrated into the polymer film in a second solution processing step), showed preferred face-on chain orientation resulting in higher short-circuit currents, which are consistent with the increased hole mobility of face-on oriented polymer chains[38].

Previous reports have suggested that the Flory-Huggins solution theory is suitable to describe polymer donor-acceptor mixing behaviors in distinguishing phase separation regions. Investigating the optimal donor-to-acceptor (D:A) ratio for creating a favorable phase separation structure is beneficial for enhancing the generation and diffusion of excitons[35]. The molecular weight of the polymer plays a crucial role in influencing aggregation tendencies, phase separation behavior, and the orientation of the main polymer chains. Manipulating the processing and engineering of the active layer is a simple and commonly employed approach to enhance the morphology of the blend film[34]. However, films produced through a single solvent-based spin-coating technique often exhibit inadequate morphology, including increased phase separation, reduced alignment of polymer chains, and compromised phase purity, resulting in unsatisfactory photovoltaic performance[35]. Fortunately, the application of solvent engineering, the inclusion of additives, controlled thermal annealing, and solvent vapor treatment have proven effective in optimizing the morphology of blended films[36]. Solvent engineering plays a critical role in controlling the morphology of the polymer blends used in the active layers of PSCs. Solvents affect both the thermodynamics (the phase diagrams) as well as the kinetics of the phase separation of the different polymer blend components. For example, by tuning the polymer-solvent interaction and the boiling point of the solvent, one can control the kinetics of phase separation that occurs during drying, and ultimately determine the morphology in the solid state. A faster phase separation/drying will maintain a more randomly mixed morphology structure, with smaller domains, closer to the solution state, while a slower phase separation will produce films with larger separated polymer domains, or crystallites, because the polymer chains have a longer time to rearrange in the most thermodynamically favored morphology[39,40]. Furthermore, the adjustment of polymer side chains and regioregularity (the degree to which a polymer's repeat units are derived from the same isomer of the monomer) offers a viable strategy for exerting control over the conformation, orientation, and stacking of polymers[35]. Scientists often use a 2D molecular weight optimization matrix to identify a target, intermediate blend of the two donor and acceptor regions, highlighting the need for a balanced aggregation strength between the two to achieve optimal morphology for high-performance[35].

From an architectural perspective, the cell's active layer can exist in a binary structure with two distinct donor and acceptor polymers or it can exist in more complicated orientations with the addition of either more donor or acceptor polymers. Recently, the NDI-based polymer acceptor N2200 has emerged as a pivotal component in high-performance OPV cells in part due to its high electron affinity and excellent electron transport capabilities[35]. To ensure that optimal blend morphology is achieved, extensive research is done on solvents and how their interaction with the polymers impacts aggregation within the cell.

The degree of regioregularity and the molecular weight of the polymer molecules used in the active layers have a significant impact on the morphology and performance of PSCs, by affecting both intrachain and interchain interactions[41–44] .

From an intrachain interaction, perspective, a high degree of regioregularity favors planar conformations of polymer chain segments, which in turn result in highly conjugated polymer chains with high charge delocalization and transfer. From an intramolecular interaction perspective, a high degree of regioregularity, provides a high degree of order among polymer chains, favoring crystallinity and molecular orientation and stacking[43]. Additionally, the pursuit of optimal molecular weight led to the discovery of a ”sweet spot” which, when achieved for both polymer donor and polymer acceptor, resulted in improved PCEs and better intermixing[34]. Modeling has also shown that variation of polymer molecular weight affects intrachain and interchain interactions. Molecular weight affects the conformation of the polymer chains and therefore can affect both intrachain interactions, such as chain folding and molecular orientation and stacking, as well interchain interactions, such as crystallization and solubility. Increasing molecular weight decreases polymer solubility and favors crystallization (lower number of free chain ends and high connectivity between crystallites). In turn, this determines phase separation and morphology within the cell, both of which are key aspects for the generation and diffusion of excitons[36]. Thus, tuning donor and acceptor polymers to have optimal regioregularity and molecular weight are important considerations for engineers looking to improve crystallinity and orientation with OPV cells[35].

From the study by Zhou et al.[35] shown in Table 3, it could be seen that certain blends and compositions of donors and acceptors resulted in more favorable molecular stacking and order within the cells, thus boosting observable metrics, most notably parameters such as short-circuit current density and the PCE. For instance, an OPV cell consisting of an active layer of J51:P(NDI2OD-T2): was able to boost its JSC (14.18 mA/cm2 to 17.37 mA/cm2) and PCE (8.27 to 9.29%) with the addition of a PTB7-Th polymer in the donor blend[35]. However, such advancements achieved from turning a binary cell into a ternary resulted in drawbacks in fill factor measurements as well as a general lack of consistency among other polymer blends[45]. For example, the OPV cell PTzBI-Si: P(NDI2OD-T2) recorded the highest PCE at 11.76% among the rest of the tested devices despite having a ternary cell version PBTA-BO + PTzBI-Si:(P(NDI2OD-T2)), which only recorded a PCE of 10.12%[35].

The successful pairing of N2200 with various polymer donors, such as PTB7-Th, PTzBI-Si, and PBDB-T, has led to remarkable PCE enhancements. As such, the use of polymer donors with conjugated side chains has improved the molecular orientation in All-PSCs with respect to the D/A interface, while polymer donors lacking this structural feature have shown poorer performance as a result of favored edge-on orientation. Face-on orientation between the substrate and donor : acceptor interface has proven to be more efficient for charge separation and transport. These polymer blends, in addition to solvent engineering and morphological control strategies, have paved the way for efficient charge separation, favorable interpenetrating networks, and boosted All-PSCs performance, with PCEs reaching up to 11.76%[35].

Discussion

General Discussion

Organic Photovoltaic cells present both strengths and challenges that impact their feasibility and potential widespread adoption. Key strengths include their sustainable cost production, reduced environmental impact during creation, lightweight and flexible nature, and versatility for various industrial applications. One of the most appealing aspects of OPV cells is their potential for low-cost production using solution-based processes, which can lead to reduced manufacturing costs compared to traditional silicon-based solar cells. This advantage aligns well with the growing demand for affordable and accessible renewable energy sources. Additionally, the lightweight and flexible characteristics of OPV cells make them suitable for integration into a wide range of applications, including wearable devices, building-integrated photovoltaics, and other unconventional energy-harvesting platforms. Furthermore, the absorption spectra of organic materials can be finely tuned through chemical modification, allowing for customization to match specific light sources or applications.

However, OPV cells do come with certain drawbacks, primarily centered around their power conversion efficiency compared to traditional inorganic solar cells. While impressive strides have been made in increasing the efficiency of OPV cells, they generally exhibit lower PCEs when compared to silicon-based cells. This lower efficiency can limit their competitiveness in high-power demanding applications and scenarios with limited available space for solar panels. Another challenge lies in their reduced durability and performance degradation when exposed to environmental factors such as moisture, heat, and UV radiation. The organic materials used in OPV cells are more susceptible to degradation over time, leading to a shorter operational lifespan compared to their inorganic counterparts.

In the pursuit of overcoming these challenges, recent advancements in OPV cell technology have demonstrated the potential for improving their efficiency and stability through innovative engineering strategies including modifications of side-chains, interfacial layer engineering and optimization of polymer blends. In addition to addressing their limitations, OPV cells can also find success in specific applications by maximizing their strengths to offset their limitations. For example, maximizing their tunable and customizable absorption spectra can enable designing multi-junction OPV devices that can efficiently harvest solar energy over a broader spectrum of light, leading to improved overall efficiency, particularly under lower illumination conditions where traditional solar cell tend to suffer. In yet

Table 3 Blend compositions and operating metrics of recent N2200 based All-PSCs. VOC = Open-Circuit Voltage, JSC = Short-Circuit Current, FF = Fil Factor, PCE = Power Conversion Efficiencies[35].

Acceptor	Donor	Architecture	VOC (V)	JSC (mA/cm2)	FF (%)	Highest PCE (%)
P(NDI2OD-T2)	P3HT	Binary	0.52	1.41	29	0.21
P(NDI2OD-T2)	PBDTTT-EF-T	Binary	0.794	13	55.6	5.73
P(NDI2OD-T2)	PPDT2FBTH	Binary	0.85	8.98	47	8.74
P(NDI2OD-T2)	J51	Binary	0.83	14.18	70.24	8.27
P(NDI2OD-T2)	PTzBI-Si	Binary	0.85	16	77.9	11
P(NDI2OD-T2)	PTzBI-Si	Binary	0.88	17.62	75.78	11.76
P(NDI2OD-T2)	PTzBI-Si	Binary	0.865	15.76	73.76	10.1
P(NDI2OD-T2) + PNTB	PBTA-BO	Ternary	0.84	15.77	74.9	10.09
P(NDI2OD-T2)	PBTA-BO + PTzBI-Si	Ternary	0.836	15.64	77.92	10.12
P(NDI2OD-T2)	J51 + PTB7-Th	Ternary	0.81	17.37	63.7	9.29

another example, optimizing their light weight can enable packing sufficient power in applications such as wearables, where space and weight are very limited and therefore more challenging for the traditional, heavier and bulkier, silicon-based solar cells.

Side Chain Modifications Outlook

In the realm of non-fullerene acceptors (NFAs), strategic side-chain alterations have proven adept at capturing solar photons effectively, yielding high output current densities. These modifications have also exhibited potential in mitigating radiative and non-radiative energy losses, bolstering the efficiency of NFA-based devices. Turning to NFA BTP-4Cl, side-chain engineering emerges as a pivotal player, enhancing solution processability crucial for practical applications in the industry. The delicate balance achieved by tuning flexible side chains contributes to optimizing charge transport while retaining solution processability, a critical consideration for performance optimization.

As these modifications become more prevalent in the industry, so too will the deposition method, which encompasses spin-coating and blade-coating as prominent options. Spin-coating provides fine control over film thickness and uniformity, favoring research with its speed and precision. However, it can lead to material wastage and challenges in mass production uniformity. On the other hand, blade-coating suits large-scale manufacturing due to its roll-to-roll process, minimizing material wastage and simplifying production logistics. Yet, achieving consistent film thickness is more complex, requiring optimization for uniformity. The choice between these methods balances precision and scalability, influencing the impact of side-chain engineering on OPV cell performance and implementation.

Interfacial Engineering Outlook

Introducing interfacial engineering through the incorporation of either conjugated polymers like PEDOT:PSS or fullerene derivatives has demonstrated a promising avenue for enhancing organic photovoltaic cell performance. Further research and investment in this technique ought to continue as observable gains in optimizing charge carrier collection efficiency could be seen. This boost in performance is particularly notable in comparison to the relatively lower PCEs achieved by commonly used PDI-based cells. As compared to side-chain modifications, IFLs primarily focus on tailoring the interface between the active layer and electrodes to improve charge carrier selectivity. IFL engineering by nature is comparatively more limited in its ability to revolutionize material synthesis and process scalability. Challenges also exist in achieving uniformity and precision in the composition of each IFL. However, considering that IFL production is already in line with established large-scale fabrication techniques, continued exploration of novel materials and designs will further optimize charge transport and layer consistency, ultimately enhancing the overall stability and efficiency of these cells.

Morphology Outlook

Cell morphology and molecular orientation within the active layer of OPV devices have emerged as critical determinants of performance. The optimization of blend morphology through solvent interactions and the identification of the optimal molecular weight have collectively led to improved power conversion efficiencies and enhanced intermixing of materials. However, the transition from binary to ternary structures may result in trade-offs, impacting fill factor measurements and introducing inconsistencies among various polymer blends, thus emphasizing the need for greater and more specialized research on individual cell compositions.

Comparing these findings to the prior strategies of side-chain engineering and interfacial layer alterations, it becomes clear that morphological optimization plays a complementary role in enhancing OPV cell performance.

Unification of the Three Strategies

While side-chain engineering and IFLs primarily target charge transport and carrier selectivity, morphology manipulation targets intermolecular interactions, phase separation, and donor-acceptor intermixing. The combination of these approaches could offer a comprehensive enhancement strategy, addressing multiple facets of OPV cell efficiency and stability: blade-coating techniques taken from side-chain engineering offer greater large-scale fabrication potential; IFLs grant the largest increases in PCE performance; Optimal morphology blends grant greater cell stability and phase separation. Furthermore, the field is witnessing advancements in sustainability, as ongoing research delves into materials that are both environmentally friendly and exhibit improved operational lifetimes. As such, manufacturers ought to weigh the considerable number of steps often involved in optimization procedures in the grand scheme of their carbon footprints. As discussed in the Introduction, given their low embedded energy materials of construction, OPV can have a carbon footprint that can be > 20 times lower than that traditional silicon-based cells. This highlights the importance of material choices when designing and optimizing the cell. Furthermore, by controlling interfacial layers and blend morphology one can increase the cell stability, and therefore the operational lifetime, which can result in a reduction of carbon footprint per unit of energy by a factor proportional with the increase in the cumulative energy output of the longer lasting cell.

Looking ahead, questions remain regarding the scalability of these techniques, as well as the long-term stability of the achieved improvements. Scalability questions are primarily linked to the fact that a significant part of the research data has been generated on small-area OPVs, and historical data has shown that large-area OPVs typically lag in performance. However, the scalability questions can be addressed by integrating these techniques together to enable scaling up to and testing large-area OPVs. For example, the potential of side-chain modifications in that direction can be leveraged to enable high-scale developments for the other two techniques. Stability questions, although addressable, as discussed here about operational lifetime, are primarily due to relatively limited data on long term stability studies, which should continue to be an area of enhanced research focus in future.

Conclusion

In this study, we explored the potential and challenges of OPV cells, an emerging renewable energy technology. While OPV cells offer sustainable, cost-effective, and flexible energy solutions, their lower power conversion efficiency compared to traditional solar cells and vulnerability to environmental factors remain obstacles. Our investigation focused on systematic analysis of three optimization strategies to address these limitations: side-chain, interfacial layer, and morphology engineering.

We found that subtle changes in polymer chain length impacted current generation and charge extraction efficiencies. Additionally, the choice of deposition method influenced performance, highlighting the balance between precision and scalability. Incorporating interfacial engineering with materials like PEDOT:PSS and fullerene derivatives demonstrated substantial gains in charge carrier collection efficiency and substantially high PCEs. Finally, optimizing cell morphology and molecular orientation enhanced power conversion efficiencies, albeit with less predictability. Cell stability, in addition to the improvement expected from higher PCE and lower degradative energy losses, can also be improved by leveraging the protection of the IFLs as well as controlling the blend morphology.

Based on our review, we recommend the following directions of research for further developments in improving understanding and addressing challenges related to the efficiency and stability of OPV cells:

- Further expand the research to larger-area cells to verify and validate performance at higher scale required for practical applications.

- Increase number of longer-term stability studies to better understand operational lifetime potential and limitations.

- Increase research on multi-factor strategies to further understand the interactions and potential synergies between the different strategies.

- Increase analyses on the environmental impact (LCAs) of construction materials in all stages of the life-cycle, including disposal and potential opportunities and benefits for recycling.

Through its systematic analysis, this research provided insights into how altering the composition, structure, and processing methods can influence the key metrics that define OPV cell performance for practical applications (such as PCE and stability) and what are some of the potential areas of future research that could lead to further improvements. Although a detailed cost-benefit analysis of the many materials involved in this research would not be impractical, the gathered insights into the potential that these strategies have in improving the OPV cell performance, provide a critical input into making future decisions about further investment in research as well as into large-scale applications.

Acknowledgements

I would like to thank my mentor Dr. Avery Baumann for all her guidance and support while writing this paper.

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