Non-fullerene acceptors (NFAs) have recently breathed new life into organic photovoltaic (OPVs), achieving breakthrough photovoltaic conversion efficiencies. Unlike conventional fullerene acceptors, they offer strong levels of tunability and solution-processibility that allow them to be easily exploited in the roll-to-roll (R2R) fabrication process. This has enabled a new renaissance for OPVs in the face of other photovoltaic material candidates for large-scale, high-throughput, cost-effective manufacturing. In this review, the current progress of R2R manufacturing of NFA-OPVs and the applications enabled by them are summarized. The perspectives on their research, technological, and future prospects for industry scale-up are also presented.

1. Introduction

Our world demands renewable energy more than ever and photovoltaic (PV) technologies are one of the key technologies to meet the global need of the hour for “zero emissions.” Unlike other renewable energy sources, PVs can harvest solar energy directly at the source of consumption as opposed to needing specialized “harvesting farms.” PV deployment is rapidly growing and its multiple application areas rapidly expanding.\(^1\) However, this market has been dominated largely by silicon-based PV technologies which have constraints in applications requiring flexibility, semi-transparency, and/or lightweightness.

Solution-processed organic PVs (OPVs) are a promising alternative to rigid silicon-based PVs in fabricating flexible, semi-transparent, and lightweight PV cells and modules.\(^2\) OPVs can drastically expand the number of applications that PV has to offer upon successful commercialization. The solution-processable nature of OPV materials mean that PVs can be fabricated using roll-to-roll (R2R) technologies, a widely used method popularized by the printing and coating industry to fabricate high-throughput and low-cost products. Multiple studies based on R2R fabrication of OPV modules and market studies have also been carried out proving both viability and cost-competitiveness of R2R OPVs.\(^2\) Like F-OPVs, PePVs could also be fabricated via R2R processes.\(^11,12\) OPV technology, hence took a back seat in deference to other more efficient materials.
Until the emergence of high performance non-fullerene acceptors (NFAs) which brought OPVs to a new renaissance.

NFAs were chemically synthesized compounds that were easily tunable as compared to conventional fullerene acceptors (FAs). Although more than 51,000 combinations of NFAs exist, it was not until 2016 that an NFA-based OPV (NFA-OPV) exceeded the performance of conventional F-OPVs. The first significant report for NFA materials was reported by Lin et al. who achieved a PCE of 6.8% using 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC), thereby heralding a new era of OPV technology. In the same vein, the use of the NFA, poly[(2,6-(4,8-bis-(2-ethylhexyl)-2,2'-diiodo-4H-Cyclopenta[2,1-b:3,4-b']-dithiophene)-alt-(5,5′-(1′,3′-di-2-thienyl-5′,5′-bis(2-ethylhexyl)benzo[1′,2′-c:5′,6′-c′,3′-c′]-dithiophene-4,8-dione))] (PBDB-T), a high-performance polymer with a temperature dependent aggregation (TDA) behavior, exhibited what was then record-breaking efficiencies of 11.2% as demonstrated by Zhao et al. in 2016. Since then, record NFA-OPV PCEs have risen rapidly and reached over 18%.

Arguably, the record efficiencies of NFA-OPVs still do not exceed those of PePVs. However, unlike NFA-OPVs, PePVs face other critical challenges to its commercialization that NFA-OPVs do not. For instance, the presence of the heavy metal lead (Pb) remains cause for environmental concern at end-of-life or degradation of PePVs. In addition, PePVs are highly susceptible to environmental damage and PCE performance degradation, thereby requiring enhanced encapsulation to protect them from elements such as humidity. Even if successfully commercialized, the presence of Pb will likely limit the applications of PePVs to those requiring no environmental contact.

NFA-OPVs hence represent the way forward for OPVs, allowing for a more ubiquitous uptake in applications. Compared to F-OPVs, NFA-OPVs have demonstrated high PCEs, improved stability, and printability. With this review article, we review the progress of NFA-OPVs in relation to R2R fabrication. We use the term, "R2R fabricated OPVs" to refer to all R2R processes which include printing and coating methods that will be outlined in this review. We further make the distinction between R2R-compatible (R2R-C) demonstrations for reports that use R2R methods to produce NFA-OPV devices as demonstrators and true R2R fabricated scale-up demonstrations.

1.1. A Brief History of F-OPVs

The first solution-processed F-OPVs were first reported in 1995 by Yu et al. using blends of poly(2-methoxy-5-(2’-ethyl-hexoxy)-1,4-phenylene vinylene) (MEH-PPV) as a donor and fullerene derivatives as an acceptor. The addition of fullerene derivatives into the polymer-based photoactive layers introduced an interpenetrating phase-separated donor–acceptor (D–A) network, increased D–A interfacial area in a bulk heterojunction (BHJ) and improved carrier collection efficiency by two orders of magnitude from its incumbent. Its performance was significantly better than the first solution-processed OPV with two conjugated polymers with interpenetrating polymer networks.

F-OPV development through the early years was generally incremental, although marked by a number of significant breakthroughs. Despite receiving significant attention from academia, the reported efficiencies did not attract commercial players until F-OPVs achieved its first significant breakthrough of 2.5% PCE, demonstrated by Shaneen et al., which at that time was regarded as a significant step-change improvement. This relatively high PCE was achieved by utilizing chlorobenzene as a processing solvent which produced better film morphology and topology as opposed to films-fabricated using toluene-based solutions.

The second significant breakthrough was achieved by introducing poly(3-hexylthiophene) (P3HT) as a donor polymer, which produced a PCE of 2.8%. Despite a relatively small and incremental improvement in PCE, the discovery of the P3HT:PCBM combination became the most widely used combination in OPV research. Although efforts were made to identify high-performing acceptor materials, the P3HT:PCBM combination remained the combination used by champion devices for many years. In 2006, Scharber et al. theorized a remarkable PCE of 10% (5% improvement from the highest reported PCE values) using a molecular engineering strategy using this combination.

The third significant breakthrough was marked by the discovery of other high-performance donor materials that outperformed P3HT. For instance, the polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTB), which was initially reported to achieve 3.2% PCE, achieved a further improvement of 5.5% PCE via the addition of alkane dithiols as a processing additive by Peet et al. in 2007. Since then various high-performance donor materials were developed over the next decade and the progress of OPV was driven primarily by the discovery of donor materials until the reported record plateau of 10.8%. As previously discussed, F-OPVs took a back seat in PV development in favor of PePVs until the discovery of high-performance NFAs.

1.2. Challenges and Progress of Roll-to-Roll Printed OPV

Translating R2R fabricated OPVs “from lab-to-fab” brings about unique engineering challenges that are not usually encountered in the lab environment. As such, the difference in maximum PCE achieved from scaled-up demonstrations from current stat-of-the-art demonstrations has manifested itself as what is commonly described as the “scaling lag.” Figure 1 demonstrates this phenomenon as large-scale demonstrations, despite having impressive cell and cell module sizes, are typically unable to attain the PCEs of their laboratory counterparts.

The transition from lab-scale glass devices to flexible R2R devices bring about their own unique challenges not often faced when making demonstrators. For instance, the devices described in Section 1.1 were fabricated at lab-scale via spin coating under difficult-to-scale conditions such as inert atmospheres and on glass. R2R devices are typically fabricated on flexible plastics (typically Polyethylene terephthalate (PET))-based transparent conducting electrodes (TCEs). These substrates often have poorer transparency, electrode conductivity, smoothness and thermal robustness compared to glass.

Also, in a complete R2R process, back electrodes will have to be printed as a separate layer. These back electrodes electrodes typically consist of poly(3,4-ethylenedioxythiophene) (PEDOT:PSA) with a low work function to improve hole extraction.
polystyrene sulfonate (PEDOT:PSS), a conductive polymer compositied with printed carbon or metal. Such back electrode composites often have lower levels of conductivity and generally allow for lower degrees of control to match the energy levels of that of the photoactive layer in comparison to off-line vacuum-deposited electrodes.

Furthermore, in the ever-relentless pursuit of record breaking PCEs, the amount of OPV research activity is disproportionately skewed toward batch processes such as spin-coating. While much has been said about scaling up such devices in academic reports, often the use of nonscalable or far-from-scale methods renders such record-breaking PCE demonstrations either too costly or too impractical to scale. The combination of these factors exacerbate the scaling-lag and lead to the longer commercialization times of OPV technologies.

Intrinsic material limitations of OPV materials further compound the scaling-lag issue. As discussed in Section 1.1, much of the significant breakthroughs where step-change improvements in PCEs have occurred were driven by the discovery of higher-performance donor materials. P3HT-based devices, upon their discovery and use in the donor:acceptor combination P3HT:PCBM\cite{18,26,28} remained the best performing material for years without much improvement. Among the prominent academic research groups working on R2R-fabricated OPVs at that time, Frederik Krebs and coworkers at Technical University of Denmark (DTU) who have led R2R scale-up of F-OPVs,\cite{6,7,31–33} made significant efforts to discover printable donor materials. Despite attempting the R2R processing of nearly every reported high efficiency material after publication and shortlisting possible combinations, Krebs et al. concluded that P3HT:PCBM remains the best possible performer.\cite{7} Krebs et al. did further investigations to find printable donor polymers by synthesizing over 100 combinations of electron-donating and electron-accepting molecular building blocks used in high-performance, low-bandgap donor polymers and reported that only one out of over 100 candidates showed a higher performance than P3HT in printed F-OPVs.\cite{34}

Investigations into the successful scale-up of R2R fabricated OPVs have established a number of loose requirements for ink formulations. These formulations must be 1) sufficiently robust to maintain performance in harsh drying environments, that is, multiple thermal cycles in air, and 2) tolerant to thickness variations. As will be discussed in Sections 2.2 and 2.3, NFAs offer enhanced physical properties and ease of processibility that give it a solid advantage over F-OPVs to meet these two requirements. While R2R NFAs are generally more nascent than their F-OPV counterparts, early indications in scientific literature have already shown rapid advancements in PCEs, producing more robust formulations than incumbent F-OPVs. We envision this trend to continue, rendering NFA-OPV technology to be competitive in some PV market sectors in the near future.

2. The Evolution from F-OPV to NFA-OPV

As discussed in Section 1.1, F-OPVs experienced a plateau in PCE values at the ≈10% mark. This was largely due to several intrinsic PCE limitations that are imposed by fullerene acceptors.\cite{35,36} For instance, the highly symmetrical nature of fullerene acceptors inhibits optical absorption of OPV cells in the visible region; polymer donors must therefore absorb broadly, and particularly at low photon energies. Lowering the donor:polymer bandgap eventually leads to losses through spin-triplet excitons lying below the charge transfer energy due to non-radiative recombination.\cite{37,38}
This combination of a limited spectral coverage and absorption coefficients constrains short circuit current (the largest current which may be drawn from the solar cell).

Also, fullerene acceptors exhibit fixed energy levels with strong electron affinities. As they are not tunable like NFAs, this limits the range of effective polymer donors they have complementary properties with and thus constrains the maximum open circuit voltage. Efforts to tune fullerene energy levels have had limited success largely because the use and distributions of substitution isomers lead to energetic disorder and introduces charge traps.\(^{[39]}\)

This section highlights the emergence of NFAs and gives a brief overview of their opto-electronic properties that allow them to overcome the constraints of F-OPVs. It will also discuss the physical property advantages that NFA-OPVs have over F-OPVs, including greater device longevities and ease of processibility.

### 2.1. NFAs: The Next Evolution

The emergence of NFAs has substantially disrupted the photophysics of OPVs and relieved many of the material and device design that have defined F-OPVs. These advances stem directly from the excitonic physics of OPVs, whose stepwise operation is highlighted in Figure 2a,b. Since light absorption and emission in organic semiconductors is governed by bound electron–hole pairs called excitons, donor:acceptor blends are required to separate these excitons and create free-charges. The mismatched lengthscales of exciton diffusion (typically requiring charge-separating functions to be distributed on the 5–10 nm scale),\(^{[40,41]}\) and light absorption (requiring >100 nm thickness) led to the introduction of the bulk-heterojunction (BHJ) morphology,\(^{[22,42]}\) which has dominated the development of fullerene-based OPVs.

The search for effective NFAs has included strongly absorbing materials with bandgaps both higher and lower than donor materials, including molecular derivatives of perylene diimides, naphtalimides, diketopyrrolopyrroles, benzo-thiadiazoles, as well as n-type polymers.\(^{[15,36]}\) As will also be explained in Section 3, the advent of fused-ring electron acceptors featuring indaceno[1,2-b:5,6-b’]dithiophene or IDT-type structures achieved a step-change advancement, addressing the intrinsic limitations of fullerene-based OPVs and propelled OPV performance to new levels.\(^{[15,16,44]}\) In addition, IDT-type fused-ring electron acceptors, although already efficient, have proven to be highly tunable where their optical gaps, electron affinities and ionization energies can be fine-tuned across >0.25 eV; Figure 2c,d.\(^{[46]}\) Strong optical absorption from these NFAs enables pairing with donors having complementary absorption and improved energy level offsets, usually with higher bandgap donors.\(^{[45]}\) A good example of effective pairing is in the PM6:Y6 blend which has proven one of the more complementary combinations;\(^{[46]}\) Figure 3a,b.

### 2.2. The NFA Advantage

NFAs are able to produce better PCEs and improved OPV-device properties due to a number of mechanisms. First, the complementary absorption of NFAs and polymer donors introduces hole-transfer photocurrent generation channels alongside conventional electron-transfer;\(^{[48]}\) Figure 3c,d. At certain wavelengths, the absorption coefficients of NFAs are high enough that hole transfer from the acceptor becomes the dominant channel of photocurrent generation.\(^{[43]}\) As fused-ring electron acceptors are typically chosen as the lower bandgap NFA component, their absorption is strongly resonant with the energy of the excited donor, which can facilitate rapid energy transfer that exceeds conventional exciton-diffusion electron transfer.\(^{[43,50]}\) As a result, even absorption in the donor phase mostly leads to energy transfer to the acceptor followed by hole transfer.

Next, fused-ring electron acceptors have greater tolerances for coarser phases They exhibit high exciton diffusion coefficients of over 10\(^{-2}\) cm\(^2\) s\(^{-1}\), which often corresponds to high exciton diffusion lengths (>30 nm);\(^{[47,51]}\) Figure 3a,b. Excitons hence are able to diffuse within NFAs quicker and at greater lengths. This enhanced diffusion has often been shown to arise from molecular and packing factors; the rigid planar molecular structure is associated with low reorganization energy, excellent spectral self-overlap (nearly 5 nm Förster radius), good transition dipole alignment, high chromophore density, and low energetic disorder (less than thermal energy).\(^{[47]}\)

NFAs, with its rigid fused-ring structure, also improves the physical properties of BHJ films. Figure 3e presents a comparison of the device performance of ITIC-based (NFA) and fullerene-based OPV devices after prolonged thermal annealing. A projected lifetime of 10 to 20 years have been demonstrated after suppressing chemical reactions between the ZnO and BHJ interface.\(^{[52]}\) The tunability of the molecular structures of NFAs, as will be further elaborated on in Section 3.2, allows NFA devices to be adjusted for optimal stability and efficiency. Recently, Ghasemi et al. established relationships between molecular diffusion in films.\(^{[53]}\) The understanding of these relationships will enable further development of stable NFA and donor polymer conditions for over 20 years of device stability.

The combination of facile donor–acceptor energy transfer and long-range exciton diffusion has substantial benefits for OPV function and fabrication. Whether exciting the NFA phase and diffusing to the donor:acceptor interface of the donor phase and benefitting from long-range energy transfer directly to the acceptor side of the interface, NFA blends can accomodate much coarser phase separation than their fullerene counterparts.\(^{[47]}\) These photophysical properties of NFAs account for the observed phase sizes on the order of 50 nm for optimized blends,\(^{[48]}\) and have even enabled relatively efficient bilayer and pseudo bilayer OPVs to be fabricated.\(^{[49,50,54–57]}\)

Furthermore, this tolerance for coarser phases enable NFA thin film morphologies to be optimized for high phase purity and crystallinity, which are both associated with effective charge separation, the suppression of trap-mediated recombination, and preservation of open-circuit voltage (the maximum voltage from a solar cell that occurs when net current through a PV is 0).\(^{[58]}\) Moreover, the alternating acceptor(A)–donor(D)–A–D–A electronic structure of fused ring electron acceptors such as Y6 gives rise to strong molecular quadrupole moments that can generate significant long-range band bending effects that are sensitive to crystal packing structure.\(^{[43]}\) These band bending effects can
Figure 2. Schematic of the stepwise photocurrent generation mechanism of an excitonic OPV cell, represented for the case where the donor absorbs (as in a polymer:fullerene blend). Each panel depicts the main steps of exciton photogeneration, exciton diffusion, and charge separation/generation at a donor acceptor interface. a) depicts this process spatially (zoomed in to the nanometer scale of an interface within a bulk heterojunction). b) includes the HOMO and LUMO energy level offsets needed to drive charge separation. c) Energy levels of common NFAs, along with PCBM and selected donors. d) Internal quantum energy as a function of ionization energy offset between donor:acceptor pairs, revealing a minimum requirement for >0.4 eV ionization energy offset. Reproduced with permission,[43] 2021, Springer Nature.
favor charge separation (and suppress charge recombination).\[43\] Moreover, NFAs present opportunities to finely tune crystal packing structure via appropriate selection of sidechains, other substituents and solvent processing conditions.\[59,60\]

2.3. Ease of Processing NFAs

The physical properties of NFAs make them at least or even more processible than F-OPVs. Hence, the same suite of methods developed for processing fullerene-based OPV films have been successfully applied to NFA blends and expanded upon. The use of cosolvent additives, solvent vapour annealing and thermal annealing is essential to optimizing phase separation and microcrystalline structure in F-OPVs. These approaches are at least as effective as conditions can be selected to enhance crystallinity with less concern that phase sizes may then exceed diffusion lengthscales.

The tolerance to large phase sizes also enables efficient layer-by-layer processing, in which the donor and acceptor are separately deposited from different solvents with orthogonal (solvent that dissolves one material and does not dissolve the other) or partially orthogonal solubilities.\[49,54–57\] Whereas depositing the top layer with a perfectly orthogonal solvent that does not swell the bottom layer could produce a sharp bilayer, some degree of miscibility tends to create stratified structures with donor-rich or acceptor-rich layers on either surface, and a coarsely phase separated blend in between. Such approaches have delivered efficiencies as high or higher than their bulk heterojunction equivalents and are functionally

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**Figure 3.** a) Complementary absorption of PM6 (donor) and Y6 (acceptor) used in a prototypical NFA blend. b) External quantum efficiency of PM6:Y6 devices as a function of film thickness. Reproduced with permission.\[46\], 2019, Elsevier. c) Fluence dependent exciton dynamics in a film of IDIC, where the accelerated decay observed with fluence is due to exciton-exciton annihilation reactions between mobile excitons. This measurement reveals an exciton diffusion coefficient of $2 \times 10^{-2}$ cm$^2$ s$^{-1}$, and an exciton diffusion length of ~35 nm. Reproduced under an open access creative commons license.\[47\] Copyright 2019, ACS publications. Efficient charge photogeneration dynamics in films of FTAZ:IDIC compared with FTAZ:PCBM blends. d) With 712 nm excitation in the FTAZ:IDIC blend, charge generation occurs exclusively via hole transfer from the NFA. Reproduced with permission.\[48\] Copyright 2018, Wiley-VCH. e) A comparison of device performance of NFA-OPV and F-OPV devices after thermal annealing at 100 °C. Reproduced with permission.\[14\] Copyright 2016, Wiley-VCH. f) Device structure and g–i) performance of bulk heterojunction (BHJ) and pseudo bilayer (PB) OPV devices comprising PM6 (donor), and N3/PCBM (acceptors). Reproduced with under an open access license.\[49\] Copyright 2021, Nature Springer.
similar, but with a greater degree of control over deposition parameters.\textsuperscript{[49,54]}

Additives that co-crystallise within NFA blends to create ternary or quarternary blends have also proven effective.\textsuperscript{[61,62]} Such additives can be highly compatible with their NFA hosts such that they specifically pack together at the molecular level rather than phase separate. In this way, these additives can modulate the crystalline structure, as well as opto-electronic properties, potentially even contributing to absorption themselves.\textsuperscript{[61,62]}

Ternary and quarternary blends have strong advantages for NFA-OPVs and will be discussed in the following sections.

3. Classes of NFA Materials

NFA-OPVs as previously-mentioned, have the potential to be a game changer for R2R technologies with its unique absorption range and opto-electronic properties. One vital component to achieving good NFA-OPV system success is achieving optimal donor:acceptor pairing. By matching HOMO/LUMO energy levels, losses that may occur during exciton formation and electron movement can be minimized. Additionally, enhanced morphology and molecular orientation can also be achieved by designing a molecular structure suitable for a donor. Doing so ensures that light in the UV-visible absorption region that a solar cell will be efficiently absorbed and converted into energy. In this section, we discuss common donor:acceptor materials relevant to R2R NFA-OPVs that have been previously demonstrated.

3.1. Common Donors for NFA OPVs

The early transition reports from FA to NFA devices saw a continuation and pairing of common FA donors with NFAs. This often led to poor energy level matches and consequently poor device performance. Early NFA R2R work from 2013 to 2015/2016 where initial reports saw efficiencies of <1%.\textsuperscript{[63–67]}

Since then, multiple candidates have emerged as leading donors for NFAs, including PBDB-T, J51 and PTBs and their respective derivatives (Figure 4).

PBDB-T and its related derivatives have been widely used as a donor material in NFA-OPVs. PBDB-T derivatives are conjugated polymers with the combination of 2-alkylthiophene-substituted benzo[1,2-b:4,5- b0] dithiophene (BDT) and 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethyl-hexyl)benzo-[1,2-c:4,5-c0] dithiophene-4,8-dione (BDD).\textsuperscript{[68,69]} They function well as donor material for a variety of reasons. First, the polymer backbone

![Figure 4](a) PBDB-T, (b) PTB7, PTB7-DT, PTB7-Th, (c) J51, J61, J71, FTAZ.

Figure 4. The chemical structures of representative donors used in NFA-OPVs. The different classes are a) PBDB-T and derivatives, b) PTBs and derivatives, c) J51 and derivatives.
and side chains can be easily modified to tune the absorption spectrum, energy level and aggregation behavior of the overall photoactive layer. For instance, a common donor:acceptor match for NFAs is PBDB-T:IT-4F. However, energy level mismatches between PBDB-T when paired with IT-4F often produces poor device performance (~8% PCE).\[70\] Fluorination and chlorination of the thiophene unit of the benzothiadiazole (BDT) side chains can lead to the much improved PBDB-T:2F (PM6) and PBDB-T:2Cl (PM7) and increased PCEs of >13%.\[71,72\] PBDB-T isomers also tend to aggregate, thereby forming spontaneously-disordered orientations. These spontaneously ordered orientations impede non-radiation carrier recombination, thereby improving the performance of NFA devices.\[73-76\]

JS1 and its derivatives share a common component, BDT, with PBDB-T and are another series of commonly-used donor polymers.\[77-79\] In conjunction with BDT, other components include fluorine-substituted benzotriazole (FBTA) acceptor unit and the thio-phen-π-bridge. Modifying the side chains located in the BDT and FBTA components allows for tuning of the HOMO/LUMO energy levels, molecular packing, and blend film morphology of JS1 derivatives.

PTBs are another series of conjugated polymers that are widely used in NFA-OPV. Their derivatives include PTB7, PTB7-DT, PTB7-Th, and other PTB varieties. PTBs are made up of alternating benzothiadiazole (BDT) and thienothiophene (TT) units along the π-conjugated backbone with various side chains.\[80\] PTBs typically have a narrow bandgap with peak absorption at 550–750 nm.\[81\] Recent reports have shown that both fullerene and non-fullerene acceptor PVs utilizing PTBs have reported PCEs of ~14%.\[82-84\] with the current R2R fabricated NFA demonstration at a record of 13.5% by Lee et al. with a ternary blend of PTB7-Th:PC71BM:Co8DFIC\[85\] in a donor:FA:NFA configuration. We note that the record of 13.5% is achieved utilizing slot-die coating on glass (i.e., using a R2R-C method) while the record efficiency reported on a flexible paper substrate is 9.6%.

### 3.2. NFA Materials

NFAs have the advantage of being able to optimize parameters related to PCE through various molecular structure changes. Compatibility with the donors can be improved via structural modifications.\[86\]

For instance, matching the same HOMO/LUMO energy levels will reduce losses that may occur during exciton formation (non-radiative recombination), and enhanced morphology and molecular orientation can be achieved by designing a molecular structure suitable for a donor. Their molecular structure allows for the targeted expansion of their light absorption spectrum and the possibility of lowering their energy barrier for charge transfer, thereby leading to an improvement of the optoelectronic properties of NFA-OPVs. This is unlike their fullerene counterparts whose 0D structure makes modification difficult. This can be illustrated by the example depicted by comparisons of common fullerene acceptors with non-fullerene acceptors in Figure 5a,b. NFAs are generally a sub-unit with a backbone and side chains. The backbone can be modified by changing the atoms constituting the fused cyclic ring, such as by introducing a heteroatom into the fused ring, in order to tune its wavelength response; Figure 5b. Alkyl or alkoxy groups can also be added to the side chains in order to make the NFA more soluble. When paired well with the donors mentioned in Section 3.1, they are capable of producing higher PCEs than their fullerene incumbants.

Although a large number of NFAs exist in academic literature, only a select few and their derivatives have ever been used in NFA-OPV devices. Even fewer still have been translated into R2R NFA-OPVs.\[87\] The NFAs that have been successfully demonstrated on R2R OPVs can be generally divided into three categories of first, fused cyclic ring (FCR)-based Small molecules, second Indacenodithiophene (IDT) and hexacyclic indacenodithieno[3,2-bj]thiophene (IDTT)s-based NFAs and Naphthalene diimide (NDI)-based small molecules.

#### 3.2.1. IDT/IDTT-Based NFAs

As mentioned in Section 2.1, the discovery and introduction of IDTs were the key advancement in the overcoming of the intrinsic limitations of F-OPVs. Examples of IDT and IDTT-based NFAs include ITIC, IEICO, and their many derivatives. These polymers are based on a seven-ring fused core with four hexarylphenyl groups substituted.\[88\] Figure 5c depicts the molecular structure of IDT and IDTT-based NFA derivatives. Modification of the side-chains can produce different ITIC and IEICO derivatives, including IEICO-4F IT-2F, IT-4F, ITIC-2Cl, ITC-2Cl, IDIC, and m-ITIC. ITIC and its derivatives are now the most widely-used in NFA-OPVs, producing outstanding performance as it marked the start of a generation of OPVs using electron-accepting small molecules. HOMO/LUMO energy levels of ITICs are about ~5.48 eV\[89\] making it easy to work in tandem with polymers with small bandgaps and thus produces increased charge separation efficiency and reduced energy losses. ITIC has an absorption range of 600–800 nm with a peak at ~700 nm,\[89\] thereby allowing absorption from the visible to the NIR region. ITIC can easily be paired with other materials in order to create a wide light absorption range. ITIC exhibits good physical properties as well with no energy losses found when exposed to 100 °C heat for 250 h.\[90\] R2R NFA-OPVs using IT-4F, a fluorinated derivative of ITIC, as an acceptor generally perform better than systems using unmodified ITIC with ITIC systems struggling to hit 10% PCE\[90-95\] where IT-4F regularly achieves ≥13% PCE.\[96,97\] It is hence expected that reports on R2R NFA-OPVs from 2019 onward have seen a shift toward using IT-4F as the main derivative of ITIC. IT-4F has also been demonstrated to be effective as part of a ternary mixture of PM6:Y6:IT-4F by An et al.\[91\] Less popular than ITIC derivatives but increasing in significance is IEICO-4F, a fluorinated derivative of the IDTT-based NFA IEICO, which has also been used as both a lone acceptor or part of a ternary mixture.

#### 3.2.2. FCR-Based Small Molecules

A good example of a commonly used FCR-based molecule is Y6. Y6, which is sometimes referred to as BTP-4F is a
flourinated FCR acceptor with an electron-deficient core. Figure 5d depicts the molecular structure of Y6 and its commonly-used derivatives for NFA-OPVs. Y6 has a broad light absorption range of 600–950 nm and peak absorption at \(\approx810\) nm. Molecular modification of Y6 can even expand the range of its spectrum, to 1100 nm, giving it absorption capabilities even in the nonvisible, IR range.\(^{[46,99]}\) The benzo-thiadiazole core of Y6 allows it to pair well with PBDB-T-2F (PM6) which has a complementary light absorption range of 400–650 nm.\(^{[75]}\) The PM6:Y6 pairing consistently brings about PCEs \(\gtrsim16–17\) %\(^{[75,100–103]}\) and earning its place as the best possible single donor:NFA combination for R2R NFA-OPVs to date.\(^{[34]}\) This PCE translates well into the realm of R2R scale-up with a record R2R-C demonstration PCE of 16.35% currently held by Sun et al.\(^{[104]}\) As mentioned in Section 3.2.1, PM6:Y6 can also be incorporated into ternary mixtures for R2R scale-up for combination such as PM6:Y6:IT-4F\(^{[21]}\) and N2200.\(^{[105]}\) Improvements in PCE related with PM6:Y6 are often due to a broadening of the absorption spectrum and improved heterojunction morphology, which ternary mixtures attempt to achieve.

3.2.3. NDI-Based Small Molecules

While ITIC and Y6 derivatives make up the majority of NFA materials that have been widely reported, there exists other less commonly used polymer materials with functional core groups that have been used in R2R NFA-OPVs. The most representative of these materials is N2200, a NDI-based small molecule; Figure 5e. N2200 has a relatively narrow bandgap of \(\approx1.5\) eV with HOMO/LUMO levels at \(-5.45/-4.00\) and two absorption ranges at 300–450 nm and 500–800 nm, respectively, thereby making responsive from the UV–vis to the NIR region. While N2200 can be used as an NFA\(^{[106]}\) on its own, the incorporation of N2200 into ternary mixtures produces optimized morphology and more balanced charge transport which often translates into improved PCE. For instance, Dong et al., upon introducing N2200 into a PM6:Y6 mixture to produce the ternary blend of PM6:Y6:N2200 saw an improvement in PCE from 13.2% to 16% while maintaining the same blade coating process for deposition of the photoactive layer.\(^{[105]}\)
4. Current Demonstrations on R2R Compatible Fabrication Methods for NFA-OPVs

Several methods have emerged over the years as proposed methods scale-up fabrication of NFA-OPVs. As a simple lab process, spin-coating has been established as the dominant method in NFA-OPV fabrication scientific demonstrations and has currently achieved the highest reported PCEs of 18.86%[107]. However, its simplicity that underlines its success in scientific demonstrations makes inherently challenging to scale up as an R2R method due to its nature as a batch process.

R2R deposition methods can include both unidirectional coating methods and printing methods or even a combination of the two. While deposition methods may vary, ideal R2R processing conditions for large area modules will involve either partially coated, partially printed, fully coated, fully-printed or hybrid approach in an inline configuration. The holy grail of such an approach is the ability to deposit all layers (photoactive layers, electrodes, etc.) in a single coating/printing pass. Krebs et al. demonstrated this approach in 2010 with a hybrid system of combining slot–die coated, flexographic printing and screen printing.[108]

With NFA’s emergence as a prominent photoactive component, R2R-C fabrication methods have been used to demonstrate NFA-OPVs, with the majority of such R2R methods reaching its renaissance post 2018. Figure 6a depicts the major demonstrations of R2R NFA-OPVs since 2015 to present day grouped according to their deposition methods. Current R2R demonstrations such as unidirectional coating methods and printing methods have achieved PCE values close to the records produce by spin coating and are closing in on the scaling lag. As discussed earlier, there have been only small number of

Figure 6. a) A comparison of different R2R methods for NFA-OPV scale-up from 2015 to 2021. b) Comparison of the number of demonstrations with regards to deposition methods. c) A comparison of R2R NFA-OPV demonstrations according to size classifying demonstrations into “lab-scale,” “proof-of-concept,” and “large-area” demonstrations.
reports demonstrating R2R NFA-OPVs. The summary of demonstrations depicted in Figure 6 and Table 1 include only NFA-OPV demonstrations by fabrication methods that can be used with R2R process.

The primary advantage and ultimate goal of R2R methods are their ability to fabricate larger industrial-scale NFA-OPV modules. Figure 6b highlights the different reported demonstrations grouped into smaller “lab-scale,” larger “proof-of-concept,” and “large-area” with their reported PCEs. Record PCE values and the majority of the demonstrations are still at the lab-scale with the majority of the devices reported being 1 cm² in active area or less. A number of reports have achieved proof-of-concept demonstrations, notably by Meng et al. (PCE = 8.9%, size = 15.00 cm²),[94] Liao et al. (PCE= 10.40%, size = 20.40 cm²),[109] and Lee et al. (PCE= 9.6%, size = 30.00 cm²).[85] At the end of the spectrum are large-scale demonstrations with the record size of 80.00 cm² achieved by Han et al. at 5.25% PCE.[110] Other notable large-area demonstrations include Strohm et al. (PCE = 5%, size = 60.00 cm²)[111] and Anderson et al. (PCE = 9.32%, size = 55.50 cm²).[97] The general and expected observation as that lab-scale demonstrations often have higher PCE levels while achieving larger cell and module sizes often report lower levels largely because of the more complex engineering parameters required for R2R scale-up. Lab-scale devices, which are generally small scale (≤4 cm²) benefit from ease of fabrication and avoid the deleterious effects of engineering features such as increased series resistance, device shorting due to unwanted electrode contact, uneven deposition of photoactive layers and solvent evaporation due to high levels of coating/printing functional fluid exposure. It is also easier to control ambient temperatures in lab-scale devices, for instance having fabrication apparatus located inside glove boxes.

Demonstrations consisting of larger device areas and structures often have fabrication systems in ambient environments and suffer from the above-mentioned engineering issues. For instance, ensuring completely short-free devices and completely even distribution of photoactive materials across 80 cm² modules is a highly challenging proposition.

Of the different R2R deposition methods, unidirectional coating methods such as slot–die and blade coating dominate the field disproportionately due to their simplicity and an intrinsically low PCE loss in large-area devices due to the relatively low-conductivities of transparent conducting electrodes; Figure 6c.

Of all the methods, blade coating is the predominantly chosen R2R method for demonstration; Figure 6c. However, most larger area proof-of-concept and large-area demonstrations have in-fact been carried out using slot–die coating as can be seen in Figure 6b. This phenomenon can be explained largely by the easier and simpler set-ups that blade coating presents. Despite having a more complex R2R set-up, slot–die systems are able to produce well-defined linear patterns and as opposed to the “flood-coating” limitations of blade coating, thereby making it a more suitable method for the fabrication of large-area NFA-OPV modules and cells. These limitations and abilities will be elaborated further on in Sections 4.2.2 and 4.2.3.

The following sections highlights the different scalable methods for R2R NFA-OPV fabrication and comments on the recent advances with regard to the individual methods. In addition, the following sections will also highlight the spin-coating mechanism, why it produces high-quality and record PCEs and why spin-coating is not suited as an R2R fabrication process. Table 1 summarises the list of NFA-OPV demonstrations according to their photoactive layer and deposition method.

### 4.1. Spin-Coating

Spin coating is a batch process which produces a solidified thin coating on a flat disk or plate. In scale-up fabrication, is the predominant technique employed to produce uniform thin films in industries such as coating silicon wafers in the microelectronics industry.[139] Factors such as final rotational speed, acceleration, and fume exhaust contribute to how the properties of coated films are defined. Rotation of the substrate is continually applied while the fluid spins off the edges of the substrate until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates as the film spreads. As a rule of thumb, the higher the spin speed, the thinner the film.[139–141] Film thickness is also dependent on solution concentration and the solvent. Spin-coating as a process can be divided into four stages: deposition, spin-up, spin-off, and evaporation.[140] Figure 7. Detailed deposition mechanics are available in references by Sceven.[140] Sahu et al.[143] and Lawrence.[139] Due to its simplicity and small fabrication footprint, it is also often chosen as the main coating tool of choice for many OPV reports and demonstrations and as such has also contained the high reported efficiencies for OPVs consistently above 17%.[142–144] In 2020, the reported record PCE was 17.6%[144,145] with NFA-based ternary organic solar cells. Most recently, Ke Jin et al. reported a PCE of 18.86%[147] with a D18:Cl:N3 blend. Spin coating has several advantages for producing single lab-scale devices. Film thickness is easily adjusted by changing the spin speed or by changing the deposited liquids viscosity. The ability to use small form-factor substrates such as glass slides allows for devices to be fabricated quickly and with very little material. However, large substrates cannot be spun at a sufficiently high rate to allow the film to thin. Paradoxically, even though only small amounts of material are required, only 2–5% of the material dispensed on the substrate tends to remain while 95–98% is flung off,[141] leading to high levels of wastage. As a batch process, spin coating is essentially R2R incompatible and hence is a strong contributing factor for the scaling-lag of R2R OPVs. Much is to be desired for an R2R, high-throughput system, which includes a more cost-effective use of material, the ability to deposit over large areas and the ability to repeat performance over many devices (>100 devices).

### 4.2. Unidirectional, Scalable Coating Methods

Compared to non-directional spin-coating, unidirectional coating methods show great potential for R2R NFA-OPV scale-up especially in optimizing wet-deposition thickness. Significant improvements in PCE have been reported using coating techniques that are close to the reported record efficiency of 18.86%.[147] The simplicity of these systems mean they are easily investigated and implemented, making them the most prevalent systems investigated for R2R NFA scale-up. These coating
| Year | PCE [%] | Method     | Material                        | Size [cm²] | Ref.  |
|------|---------|------------|---------------------------------|------------|-------|
| 2021 | 16.77   | Blade      | PM6:BT10-eC9                    | 0.04       | [112] |
| 2021 | 14.91   | Soft-porous blade | PTQ10:Y6 | 0.5      | [113] |
| 2021 | 13.62   | Soft-porous blade | PTQ10:Y6 | 1        | [113] |
| 2021 | 14.42   | Slot-die   | PM6:Y6                          | 0.04       | [114] |
| 2021 | 10.2    | Slot-die   | PM6:Y6:IT-4F                    | 0.1        | [21]  |
| 2021 | 15.93   | Slot-die   | PM6:Y6                          | 0.04       | [115] |
| 2021 | 13.91   | Slot-die   | PM6:Y6                          | 0.56       | [115] |
| 2021 | 13.87   | Slot-die   | PM6:Y6                          | 1          | [116] |
| 2020 | 9.63    | Slot-die   | PB-Qx:F:Y6                      | 0.1        | [87]  |
| 2020 | 10.99   | Slot-die   | PB-Qx:F:Y6                      | 0.9        | [87]  |
| 2020 | 9.5     | Inkjet     | PTB7-Th:IEICO-4F                | 0.1        | [96]  |
| 2020 | 13.61   | Slot-die   | PM6:Y6                          | 1          | [117] |
| 2020 | 9.43    | Slot-die   | PTB7-Th                         | 1          | [118] |
| 2020 | 15.6    | Slot-die   | PM6:Y6                          | 5.6        | [119] |
| 2020 | 10.2    | Slot-die   | PTB7-Th:IEICO-4F-PC71BM         | 0.88       | [97]  |
| 2020 | 13.2    | Slot-die   | PM7:IT4F                        | 0.04       | [73]  |
| 2020 | 11.6    | Slot-die   | PM7:IT4F                        | 0.95       | [73]  |
| 2020 | 11.86   | Blade      | PBDB-T:FOIC:IT-M               | 0.04       | [120] |
| 2020 | 9.32    | Bar        | PTB7-Th:EH-IDTB:R2:OEHRH      | 55.5       | [121] |
| 2020 | 15.08   | Blade      | PBDB-T:2F:Y6                   | 1          | [122] |
| 2020 | 14.75   | Soft-porous blade | PM6:Y6    | 0.05     | [123] |
| 2020 | 14.19   | Soft-porous blade | PM6:Y6    | 0.2      | [123] |
| 2020 | 11.83   | Soft-porous blade | PTQ10:IDIC | 0.05     | [123] |
| 2020 | 10.61   | Soft-porous blade | PTQ10:IDIC | 0.2      | [123] |
| 2020 | 16.35   | Blade      | PM6:Y6 (LBL)                    | 0.04       | [104] |
| 2020 | 15.23   | Blade      | PM6:Y6 (LBL)                    | 1          | [104] |
| 2020 | 14.01   | Blade      | PM6:Y6                          | 1          | [104] |
| 2019 | 15.5    | Blade      | PBDB-T:F-BTP-4Cl-12             | 0.81       | [124] |
| 2019 | 10.4    | Blade      | TPD-3F:SI1:IT4F                | 20.4       | [109] |
| 2019 | 5.5     | Slot-die   | PBDB-T:1T1C                     | 7          | [95]  |
| 2019 | 16      | Blade      | PM6:Y6:N2200                    | 1          | [105] |
| 2019 | 13.2    | Blade      | PM6:Y6                          | 1          | [105] |
| 2019 | 8.95    | Slot-die   | PBDB-T:5F:IT-4F                | 6.25       | [123] |
| 2019 | 12.5    | Slot-die   | PBDB-T:5F:IEICO-4F              | 0.04       | [98]  |
| 2019 | 11.4    | Slot-die   | PBDB-T:5F:IEICO-4F              | 0.56       | [98]  |
| 2019 | 13.64   | Blade      | PM6:IT4F                        | 0.04       | [126] |
| 2019 | 11.39   | Blade      | PM6:IT4F                        | 0.56       | [126] |
| 2019 | 5.25    | Slot-die   | SMD2:ITIC-Th                   | 80         | [110] |
| 2019 | 5.6     | Blade      | P3HT:O-IDTB:R                  | 0.08       | [127] |
| 2019 | 9.77    | Slot-die   | PBDB-T:1T1C                     | 1.04       | [94]  |
| 2019 | 8.9     | Slot-die   | PBDB-T:1T1C                     | 15         | [94]  |
| 2019 | 13.5    | Slot-die   | PTB7-Th:PC71BM:COi8DFIC         | 0.1        | [85]  |
| 2019 | 9.3     | Slot-die   | PBDB-T:PC71BM:COi8DFIC         | 30         | [85]  |
| 2019 | 14.4    | Blade      | T1:BTP-4F:12                   | 1.07       | [128] |
| 2019 | 12.9    | Slot-die   | PBDB-T:5F:IT-4F                | 0.1        | [129] |
| 2019 | 12.32   | Slot-die   | PBDB-T:5F:IT-4F                | 0.2        | [129] |
| 2019 | 9.67    | Blade      | PBDB-T:IT-M                    | 1          | [93]  |
| 2019 | 8.36    | Blade      | PTB8i:N2200                     | 0.04       | [106] |
| 2019 | 14.01   | Blade      | PM6:Y6                          | 1          | [104] |
methods include bar coating (sometimes called k-bar, Meyer, or dbar coating), blade coating (or doctor-blade coating) and slot–die coating. As opposed to a nondirectional deposition method such as spin coating, the coating methods mentioned here are unidirectional, whereby either the substrate or the deposition coating instrument is drawn in a single direction. Compared to printing and spin coating, unidirectional coating methods are relatively simple for adoption, can easily deposit thick, unbroken layers and can also be adopted for the R2R process. No matter the method, these coating methods rely on some form of liquid self-assembly moments after deposition to form a uniform film.

4.2.1. Bar-Coating

Bar-coating uses either a rod wrapped with a coiled wire or a patterned bar to deposit a uniform film material. The wire-wound rod version is known as a kbar or Meyer bar and the patterned version, a dbar. Both the bar and wire are typically stainless steel, as this allows for high levels of solvent and corrosion resistance.[146] This technique was originally developed in the early 20th century to spread carbon or wax coatings onto paper[146] and is often used in such industrial setups to apply adhesives and other wide-area coatings. The volume of the coating deposited, and hence its wet-film thickness is defined by the diameter of the wound wire. As a well-established R2R deposition method, deposition rates of up to 600 m min$^{-1}$ are possible.[146] Figure 8a shows how the bar is drawn on the substrate in order to produce a thin uniform film. Figure 8b depicts the side profile of a k-bar where the diameter of the wire meters and determines the thickness of the fluid and Figure 8c depicts a dbar. Dbar systems are significantly more expensive due to their complexity of fabrication, however, they offer the added advantage of ease of cleaning and customizable thicknesses. Although well-established as a coating method, there has only been one demonstration of bar-coating for R2R NFA scale-up to date. Lee et al. utilized a dbar to deposit PTB7-Th:EH-IDTBR:T2-OEHHR as an NFA photoactive layer achieving a reported PCE of 9.32%.[121] Significantly, the group also managed one of the largest area demonstrations to date, producing a module with an active area of 55.5 cm$^2$. Despite having only one demonstration, bar coating remains a highly promising method of fabricating large area devices despite its drawback of being solely a “flood-coating” method.

| Year | PCE [%] | Method | Material          | Size [cm$^2$] | Ref. |
|------|---------|--------|-------------------|--------------|-----|
| 2019 | 15.23   | Blade  | PM6:Y6            | 1            | [104]|
| 2019 | 5       | Inkjet | P3HT:O-IDTBR      | 1            | [130]|
| 2019 | 6.47    | Inkjet | P3HT:O-IDTBR      | 0.1          | [131]|
| 2019 | 15.37   | Blade  | PM6:Y6            | 0.04         | [104]|
| 2019 | 13.1    | Blade  | PBDB-T:IT-4F      | 1.07         | [132]|
| 2018 | 10.35   | Blade  | J71:ITC6-1C       | 1            | [54] |
| 2018 | 10.42   | Blade  | PTQ10:IDIC        | 1            | [54] |
| 2018 | 10.02   | Blade  | PBDB-T:IT-4F      | 0.07         | [93] |
| 2018 | 8.77    | Blade  | PBDB-T:IT-4F      | 0.07         | [93] |
| 2018 | 7.11    | Blade  | PBDB-T:IT-4F      | 0.07         | [93] |
| 2018 | 9.22    | Blade  | PBDB-T:IT-4F      | 1.04         | [133]|
| 2018 | 12.88   | Blade  | PBDB-T:IT-4F      | 0.12         | [133]|
| 2018 | 13.2    | Blade  | PBDB-T:IT-4F      | 1            | [134]|
| 2018 | 12.02   | Blade  | PBDB-T:PTB7-Th:FOIC| -           | [135]|
| 2018 | 5.49    | Blade  | P3HT:ITEBR        | 0.1          | [111]|
| 2018 | 5       | Blade  | P3HT:ITBR         | 60           | [111]|
| 2018 | 10.2    | Blade  | PBDB-T:ITIC       | 0.04         | [92] |
| 2018 | 7.6     | Blade  | PTB7-Th:ITIC      | 2.03         | [91] |
| 2018 | 11      | Blade  | FTAZ:IT-M         | 0.07         | [136]|
| 2018 | 9.8     | Blade  | FTAZ:IT-M         | 0.56         | [136]|
| 2018 | 10.1    | Painting| PBDB-T:ITIC       | 0.08         | [90] |
| 2017 | 5.1     | Slot-die| PTB7-Th:PPDIE     | 0.12         | [137]|
| 2017 | 4.24    | Slot-die| PTB7-Th:PPDIT     | 0.12         | [137]|
| 2016 | 5.21    | Blade  | PBDT-T51:PPDODT   | 6.9          | [138]|
| 2016 | 0.65    | Slot-die| P3HT:PhDMe(DPP)2 | 1            | [67] |
| 2015 | 3.2     | Blade  | PII-T-PS5:PTP     | 0.04         | [66] |
| 2015 | 1.02    | Slot-die| PBDDTT-C-TDC-IDT2T| 1            | [65] |
4.2.2. Blade Coating

Blade coating (also known as doctor-blade coating) is a material "flooding" method designed for large-scale fabrication and has already been widely utilized in the solution-processed solar cells and Li-ion batteries. It is generally used for applications which require no patterning and require simple thin-film material deposition. Blade coating usually consist of three steps: depositing solutions in front of the coating tool, moving the coating tool or substrate to spread the solution, and drying the substrate gradually; Figure 8d,e. Such a process makes blade coating suitable for large-scale successive fabrication with minimal wastage of effective materials. Film morphology is modulated by the self-assembly of functional materials in doctor-blade coating and its variants. The key parameters in doctor-blade coating are the solution concentration, substrate temperature, coating speed and the distances between coating tools and substrates. Blade coating is also the most popular form of coating used for deposition of photoactive layers in demonstrations and currently holds the record of 16.35% by Sun et al. using PM6:Y6 in a layer-by-layer deposition pattern. In this demonstration the different components of photoactive material are sequentially doctor-bladed, from donor PM6 solution and acceptor Y6 solution using chloroform as a solvent. Indeed, large-area demonstrations have been made possible with blade coating, albeit at the cost of PCE as compared to lab-based methods. Strohm et al. demonstrated a 60 cm² module using blade coating with a reported PCE of 5%. While blade coating serves as an appropriate model technique for large area coating, there are however several challenges that are required to be overcome. Despite its simplicity, blade coating’s primary drawback is its inability to have an in situ coating source, thereby relying on an external means of depositing raw material before metering. As a result, demonstrations are often small with Sun et al.’s device currently being 0.04 cm² in size. Scaling up blade coating would mean that engineering parameters such as viscosity changes with evaporation would have to be taken into account and optimized. In addition, as a flood-based system, blade coating usually requires multiple secondary steps such as laser scribing and expensive inline laser systems in order to produce linear patterns.

4.2.3. Slot–Die Coating

Slot–die coating bears strong similarity to the blade process except that it contains a flow channel inside the blade, thereby allowing for continuous solution supply in a closed solution feed system; Figure 8f,g. Deposition occurs through the formation of a meniscus between the tip of the coating head and substrate. The coating head typically consists of two metal blocks, a shim situated inbetween these two blocks and an optional meniscus guide. This versatile deposition technique has multiple practical advantages over blade coating, including the ability to pattern continuous linear stripes which makes it both the most likely method for scale-up as shown in Figure 6c and is now the second most experimented method used for R2R fabricated NFA-OPVs; Figure 6b. For conventional OPVs, slot–die remains the technique of choice for large-scale R2R fabrication. It should be noted that flood-based methods like blade coating still dominate because of its simplicity and cost-effectiveness in set-up. However, unlike blade coating, slot–die coating is a closed-feed system, the system is lossless, leading to less material wastage and simpler control of wet-film thickness. The thickness of the wet film can be precisely controlled via solution feed rate control. In addition, the closed-feed system also prevents contamination and excessive solvent evaporation compared to open-reservoir systems or open solution-feed systems such as bar and blade coating. These are problems not easily observed in lab-scale demonstrations but are highly impactful in scale-up engineering.

Commercially available slot–die systems can deposit patterns with gaps as narrow as 1 mm (1000 μm resolution). In comparison resolutions are not as high as printing methods such as gravure printing (=100 μm). It should be noted that the lower resolution of slot–die coating limits the overall geometric fill factor (GFF: the ratio of active area that produces photocurrent to the total area of the OPV module). Typical GFFs of fully printed OPVs have been reported to be between 50–70%. We recognise that innovative hybrid methods such as the combination of laser scribing and slot–die coating cab potentially produce modules of GFF ≥95%.

Once optimized, slot–die parameters can then be easily used in larger slot–die heads with minimal for scale-up with minimal additional optimization to produce additional stripe patterns for interconnected modules; Figure 8h. Due to its unique modular set-up, slot–die coating can also be innovated upon to produce step-change PCE improvements. For instance, hot slot–die coating, whereby the slot–die head is heated and temperature-controlled, has produced step change improvements in PCE levels. The technique was first demonstrated by Yan et al. and was further developed for blade coating to achieve 9.9% PCE. Vak et al. systematically investigated the effects of the substrates and the head temperatures.
Figure 8. Schematic of a) bar coating and cross-sections of a b) wireround and c) dbar, d) doctor-blade coating and its e) cross-sectional schematic and f) slot–die coating and its g) schematic of an in-situ fluid reservoir providing supply of material to the head. h) Illustrations of the scalability and patternability of slot–die coating and example of i) R2R fabricated NFA PVs with slot–die coating. j) A photograph of a R2R NFA-OPV module with an active area of 80 cm². k) Typical J–V curves of R2R printed modules. Reproduced with permission. [110] Copyright 2019, Wiley. l) J–V curve and IPCE spectrum of the first R2R processed OPV device with over 10% PCE. Reproduced with permission. Copyright 2021, Royal Society of Chemistry. Esoteric forms of coating including m) brush coating using a Chinese calligrapher’s brush and soft-porous blade coating with its (m) live photo of calligrapher’s brush, n) schematic and o) representative photograph of soft-porous blade coating. p) SEM images of the filter used as a soft-porous brush. Reproduced with permission. Copyright 2019, Royal Society of Chemistry and from. Copyright 2020, American Chemical Society.
independently and used the hot slot-die for NFA-OPV for the first time. More recently, the technique was used to achieve an impressive 15.6% PCE from the slot-die coated NFA-OPV on glass substrates and also to break the barrier of 10% PCE of R2R printed NFA-OPV as shown in Figure 8k. It is expected that the record PCE of R2R devices will increase further in near future as more recently developed materials such as D18 are experimented on. Although there have been many demonstrated R2R-C demonstrations of slot-die coating, true scale-up remains elusive. We found no examples of large-scale fabrication of slot-die R2R NFA-OPV in the literature to date and only one of R2R printed NFA-OPV module in the literature. In this demonstration, Moon et al. developed a printing-friendly donor material, SM2, which showed high performance without pre- or post-treatment. They also introduced bi-layer HTLs to recover voltage loss typically caused by energy level mismatch between photoactive layers and solution-processed HTLs/electrodes. The materials and the bilayer-HTL approach was used with an industrial R2R printer to produce 80 cm² modules as shown in Figure 8i,j. The R2R processed module showed 5.25% PCE. The efficiency is relatively high among that of R2R modules, however, the efficiency gap with glass-based NFA-OPV modules is significant and this research area should be explored more intensively to progress the technology toward commercialization via R2R manufacturing.

4.2.4. Artisanal Coating Methods

Among the many coating methods, certain artisanal methods of demonstrations that have also been posited for R2R fabrication include utilizing a Chinese paintbrush and soft-porous blade printing. Mao et al. attained a PCE of 10.1% using PBDB-T:ITIC by attaching a Chinese “maobi” directly to a three axis rig allowing effective patternable NFA deposition. Similarly, Zhong et al. achieved a highest reported PCE of 14.75% using PM6:Y6 as a photoactive layer using soft-porous blade coating as a deposition method. While novel, the cell sizes of 0.08 cm² for the maobi and 0.048, 0.5 and 1 cm² for the soft-porous demonstration indicate larger lags and challenges to scale up such methods to large-area modules and beyond despite achieving relatively high PCE of ~14.91%. As compared to other existing methods, more work is required in order to elucidate engineering parameters and scale-up challenges for such artisanal methods.

4.3. Scalable Printing Methods

While spin-coating and unidirectional coating methods current dominate the NFA-R2R space, printing as a technology holds great promise for the manufacturing of patterned printed electronics in a low-cost and high-throughput manner. Printing as a technology is now a ubiquitous technology used for graphics printing since it was first invented by Johannes Gutenberg in 1440. It has captured the imaginations of many a researcher who has used it for a wide variety of printed electronics applications including printed 2D materials, semi-conductors and conventional OPVs. Printing offers many advantages toward R2R NFAs. First, its in-line nature made of multiple inking platforms on R2R printing systems mean NFA-OPVs can be printed directly as part of fully powered printed electronics systems. NFA-OPVs can then be directly printed onto substrates, interfacing directly with low-powered printed electronics systems or even systems with printed batteries (e.g., printed IoT systems, wearables, etc.) in a single printing step.

Printing, by its nature, is also highly patternable, allowing for the fabrication of complex-patterned NFA-OPVs. These NFA-OPVs can then be more flexibly used, either as part of architectural systems or other aesthetically-pleasing applications. This has been demonstrated using conventional printable OPVs by Välimäki et al. who printed leaf-shaped OPVs using gravure and rotary screen printing. Figure 9a–c. Similarly,

Figure 9. Novel OPV printed shapes in a) R2R form in the shape of a b,c) flexible leaf and d,e) inkjet printed in the shape of a christmas tree. Reproduced with permission under open access licenses. Copyright 2015, Royal Society of Chemistry and Reproduced with permission. Copyright 2017, Springer-Nature.
Eggenhuisen et al. demonstrated christmas-tree shaped OPVs fabricated via inkjet printing,\cite{50} Figure 9d,e. Scalable printing methods have largely been used in R2R NFA-OPVs to fabricate other nonphotoactive layers such as transparent conducting electrodes (TCE)\cite{108,31,162,33} and there are presently few demonstrations of scalable printing methods with photoactive layers.\cite{133} However, scalable printing methods for the photoactive layer have been more widely demonstrated on conventional OPVs. Krebs et al. first postulated\cite{163} such printing techniques to fabricate R2R processed polymer solar cell modules in 2009. Some methods that were mentioned include using flexographic printing, slot–die coating and rotary screen printing.\cite{108} NFA-OPVs are likely to follow the same route as demand for more complex patterns and heterostructures for NFA-OPV devices emerge. Hence, although scalable printing methods are currently used for nonphotoactive components, it is natural to assume that these printing methods will eventually be used for NFA-OPVs moving forward.

It must be noted that there are a number of unique challenges that scalable printing methods present over coating systems. For instance, printing systems are much more complex than unidirectional coating methods. Parameters like viscosity and shear thinning have to be taken into account for ink design for successful NFA-OPV fabrication.\cite{159,164–166} In addition, a more complex system can also result in increased modes of failure including screen clogging or incomplete transfer on flexo and gravure systems.\cite{164} Furthermore, modern printing systems designed for graphics printing are based either on a color additive or color subtractive system of printing dots to achieve optimal colors\cite{165,166} and are not designed to print unbroken lines. The success of printed electronics systems is based on a system’s ability to print unbroken, pinhole-free devices, a parameter that is counter to the “dot-gain” systems of graphics printing. It is hence vital that printing systems be properly adapted to the needs of producing NFA-OPV photoactive films of sufficient thickness and satisfactory morphology before they can be properly scaled.

Despite these challenges, the adaptation of conventional graphic printing continues to show exceptional promise for the scale-up of R2R NFA-OPVs. This section outlines mainstream scalable printing methods that can be used for R2R scale-up for NFA OPVs.

4.3.1. Inkjet Printing

Inkjet printing is a printing technique whereby computer-controlled ink droplets are deposited in quick succession onto a substrate in order to generate a print.\cite{169} As a printing method it is well-suited to functional material prototyping as it does not require a physical mask and also allows for quick modification to print design.\cite{170} Two droplet jetting mechanisms are currently the most commonly used for inkjet printing: continuous inkjet (CIJ) and drop-on-demand inkjet (DoD); Figure 10a–c. In CIJ, a stream of charged ink droplets is continuously jetted through an electrostatic field; Figure 10a. The electrostatic field deflects the charged ink droplets to deposit onto the substrate selectively. In DoD, ink droplets are only generated on demand via piezoelectric stimulation or a thermal inkjet bubble process.

In a piezoelectric inkjet process, an electric pulse is applied to a piezoelectric material within the ink reservoir which induces a change in shape; Figure 10b. This shape deformation applies pressure on the ink within the reservoir that forces it out as ink droplets. In a thermal inkjet process (Figure 10c), ink is heated via a heating element rapidly which generates bubbles in a controlled manner, thereby propelling the ink out droplets. Among these three mechanisms, CIJ allows for the fastest jetting printing efficiency.

Despite its ability to scale, complexities in controlling ink jetting, deflection and recycling have limited the widespread application of CIJ in printed electronics applications. DoD has hence emerged as the inkjet printing technology most favored for functional printing. A key requirement for the success of DoD is the stable jetting of single droplets without the formation of satellite or secondary droplets. Satellite droplets can lead to ink deposition on unwanted areas and can also cause unwanted changes the main droplet’s trajectory.\cite{169} Ink droplet behavior is determined its fluidic properties, which can be characterized by \( Z \), a dimensionless inverse Ohnesorge (Oh) number:\[171–173]\]

To date inkjet printing is the only printing method that has been used to fabricate NFA-OPVs by depositing its photoactive layer. Most recently, Corzo et al. achieved 9.5% PCE where a PTB7-Th:IEICO-4F bulk heterojunction device was printed via inkjet.\cite{96} Due to the low viscosities (\( \xi = 30 \) mPas) required to successfully deposit the inks using an inkjet head, high boiling point solvents are often employed as carrier solvents which can often lead to aggregation issues within the inks (whereby van der Waals forces causes small particles to agglomerate or aggregate thereby blocking inkjet nozzles), or dewetting as a result of having higher surface tensions than the intended substrate.\cite{164} High surface energy substrates such as glass and polyimide hence present a printing challenge. Surfactants are often used in order to overcome these problems of wetting and aggregation/agglomeration.\cite{164} However, the use of surfactants also introduces a trade-off between print quality and device PCE as the presence of these surfactants often disrupts important networks and boundaries between donor and acceptor molecules. Maisch et al. utilized a novel approach to get around this issue by combining the inkjet printing of PEDOT:PSS to pin the contact lines of flood coated P3HT:ODTBR on glass in order to effectively create an unbroken NFA layer; Figure 10d,e. Such an approach represents the versatility of the multi-material deposition capabilities of inkjet printing in producing patterned devices even on hard-to-print surfaces.

4.3.2. Screen Printing

In screen printing, ink is deposited onto a substrate by being transferred through a mesh that are made of various materials (such as fabric, silk, synthetic fibers, or metal threads.) Patterns are demarcated via means of a photo-polymerized resin which blocks out nonimated areas, thereby allowing ink to flow through on the unblocked pores.\cite{166,174} Figure 10f depicts a schematic of a flat-bed screen printing process designed to print on a flat surface. First, ink is spread over the screen mesh in order to “flood” the pores. Next, a squeegee is drawn across
it, thereby causing the ink to shear thin and flow through the open pores. The substrate is simultaneously held in contact with the screen while the squeegee is drawn for the ink to transfer onto it. Screen printing requires shear thinning inks with a higher viscosity ($\approx 2000$ mPas) \[161,164\] in comparison to other printing methods. Most flat-bed screen systems are still simple hand-operated or machine-operated units. Such a configuration is useful when printing on substrates that cannot be fed automatically, or where a test run of a new image is required quickly. Flat-bed systems are also able to register precise prints directly on top of each other, thereby allowing for effective material positioning. \[175\] In comparison to rotary screen printing,
Flat-bed screen printing allows for better flexibility, registration, and printing interval control. This is vital in the printing of devices whereby precisely registered contacts and overlapping layers of functional materials are required for device fabrication success. Automated flat-bed screen presses are commercially available which allow for the automatic loading and unloading of substrates using feed systems. In addition, cylinder presses which are designed to be able to rotate at fast speeds for high-throughput printing are also available; Figure 10g. Rotary screen printing sees the screen, cylinder and substrate move together with the substrate while the squeegee remains stationary. While this allows for much higher printing speeds (80 m² s⁻¹) in comparison to flat-bed presses, it also means that images cannot be easily manipulated. Ink volume deposition is governed by several factors:

- screen thread count (i.e., the number of threads per unit distance)
- thread diameter, which defines the screen thickness
- the pressure, angle that also defines the area that the squeegee is in contact with the screen, and the speed of the squeegee as it is drawn.

As a highly established printing process, further details of parameters have been derived in 1990 by Owczarek and Holland in ref. [178]. At present no demonstrations have yet been found for the fabrication of NFA-OPVs using screen printing. However, conventional F-OPVs have had a strong track record of being fabricated by screen printing. The first public demonstration of screen printing conventional OPVs was reported by Krebs et al. in 2019. Multiple screen demonstrations have been reported using screen printing both as a sole method and part of an integrated inline R2R process. Automated registration systems have also been reported, thereby improving the credibility of screen printing as a good industrial process to use as a form of R2R scale-up. Figure 8h depicts the schematic of a fully R2R screen-printed PV device shown in Figure 8i by Ylikunnari et al. The use of screen printing to fabricate NFA-OPVs are likely to be a natural progression from fabricating F-OPVs.

4.3.3. Flexographic and Rotogravure Printing

Flexographic and rotogravure (also known as gravure printing) are both well-established processes that are utilized in conventional graphics printing. Figure 8j,k depict schematics of the flexographic and gravure printing processes. Flexographic printing utilises a "relief plate" in which the impression of the imaged areas stand out and erect in relation to the printing cylinder. As shown in Figures 8j,k, a relief printing plate that is flexible and pliable is mounted on the printing cylinder.

In flexographic printing, ink of a medium viscosity (1000–2000 mPas) is fed to the surface of an anilox roller (essentially a metal roller with multiple cavities) as it is rotated through the ink reservoir. Any excess ink is metered off using a doctor blade, which regulates the amount of ink that the anilox roller carries. The ink is then transferred to the printing plate before being transferred onto the substrate. Flexographic presses can run at speeds of up to ≈500 m min⁻¹. However, as it is a direct-contact process, flexographic printing is typically incapable of depositing dense layers (wet film thicknesses of up to ≈3 μm.) It achieves resolutions between 100–200 μm.

Figure 10l, m depict typical schematics of gravure printing. A gravure press printing unit consist of an ink trough which allows a metal gravure roller to rotate through it and a metal doctor blade that spans the width of the roller which meters the ink. Unlike flexographic printing, the desired image is engraved into the metal gravure roller as cells that are designed to both carry ink from the ink reservoir and deposit onto the surface of a substrate. Inks utilized for gravure printing usually have low to medium viscosities (100–1000 mPas). Gravure printing is an extremely mature printing technology, capable of delivering printing speeds of up to ≈1000 m min⁻¹. Low boiling point solvents are usually utilized as ink solvents to allow for rapid ink drying. Gravure printing is also capable of delivering dense prints (wet thickness of ≈7 μm) as it uses deeply-etched engraved cells. Printing resolutions are typically 100 μm. Nguyen et al. also presents a theoretical model representation of the printing process with details available in ref. [183, 186].

As both flexographic and rotogravure tend to form thinner deposition layers they are often not used for the photoactive layers in PV modules. Often, it is integrated inline in order to print transparent conducting electrodes (TCEs) utilizing silver nanowires (Ag NW) or nanoparticles. While likely unsuitable for photoactive deposition, flexographic printing is essential in transitioning from vacuum deposited indium-tin oxide (ITO)-based TCEs which require vacuum deposition to fully R2R printed PV units. Figure 10m depicts Ag NW rotogravure printed wires and the rotogravure cell cavities used to fabricated them by Hart et al.; Figure 10o. In both printing method’s ability to produce patterned lines make it ideal for the fabrication of large area modules and are hence essential for research into fabricating R2R NFA-OPVs.

5. Conclusion and Perspectives

This review synthesizes the research on the current position of R2R NFA-OPVs. NFAs represent the second renaissance of OPVs leading it into a new golden age of ever increasing PCEs. The flexibility of NFA systems, its tunability, widespread availability, and indeed its ability to be easily combined into ternary and different multi-component systems make it increasingly popular and a strong challenger to PePV materials. Inherent advantages allow for good solution processibility which allow them to be easily deposited via R2R lines using unidirectional coating methods and eventually patterned using well-established printing methods. This natural evolution into more complex printing methods will eventually offer faster fabrication speeds and more complex device structures. Such an evolution has already been seen in conventional OPVs as previously mentioned in Section 4.3 where novel shapes such as Christmas trees and leaves have already been demonstrated. Despite these obvious advantages there are other important research areas that contribute to the overall ecosystem of R2R NFA-OPVs. These areas also represent some of the
teething problems that R2R NFA-OPVs will have to overcome in order to achieve true commercial adoption. This section highlights these issues, potential solutions to overcome them and provides perspective as to the way forward with R2R NFA-OPV research. In addition, this section also highlights elaborates on past, previous and future commercial efforts and directions that R2R NFA-OPVs are likely to take.

5.1. Improving NFA Efficiency through New Molecular Design

Pathways that Reduce Device Losses

Although the use of NFAs has led to PCEs of 18.86%,[107] they are still comparatively less efficient than inorganic solar cells.[143] In spite of excellent optical absorption and photocurrent quantum efficiencies, NFA-based OPVs still suffer from significant voltage losses relative to optical bandgaps. Two main causes are identified for these voltage losses. First, sizeable band edge offsets of around 0.5 eV between ionization energies are required for efficient charge photogeneration.[43] These band edge offset requirements are linked to band bending effects that assist barrierless long-range charge separation, but at the expense of exciton-to-charge conversion. These band bending effects result from strong quadrupolar fields generated from NFA packing, and the question remains whether targeted molecular engineering could decrease the magnitude of band edge offset required to maintain effective charge separation. The second major voltage loss in efficient NFA-based OPVs is nonradiative charge recombination. For NFAs to improve their efficiency, nonradiative loss pathways must be identified and suppressed. A recent report by Gillett et al. shows that the majority of charge recombination under open-circuit conditions proceeds via the formation of nonemissive NFA triplet excitons.[130] In a typical PM6:Y6 blend, this fraction can reach up to 90%, reducing open circuit voltage by 60 mV, therefore allowing less power generation from the PV. Gillett et al. demonstrated that engineering substantial hybridization between the NFA triplet excitons and the spin-triplet charge-transfer excitons vastly reduces nonradiative recombination.[130] NFAs with their planar structure and easily modifiable side chains present multiple opportunities for engineering hybridization across the different viable NFAs. The work done by Gillett et al. provides a design pathway for organic solar cells with power conversion efficiencies of 20% or more. Future work will likely see increased modification via hybridization or other mechanisms of the molecular structure of NFAs in order to vastly improve the competitiveness of NFA-OPVs.

Next, the leveled cost of energy calculation (LCOE), which is defined as the ratio of the total lifecycle cost of a PV system to the total energy generated during the lifetime of the system. It estimates of the revenue required to build and operate a PV system over a specified cost recovery period and is given as[132]

\[
\text{LCOE} = \frac{\sum_{i=0}^{n} C_i}{\sum_{i=0}^{n} (1+d)^i} \left( \frac{E_i}{1} \right)
\]

where \(C_i\) and \(E_i\) are the total cost ($) and energy production (kW h) in the \(i\)th year, respectively, \(d\) is the discount rate and \(n\) is the lifetime of the system. In addition to system longevity and PCE, manufacturing cost of the system is an important factor to take into account when calculating LCOE. Figure 11a shows the LCOE distribution for 5- and 10-year lifetime ground and roof mounted OPV.[130] As depicted in Figure 11a, 5-year ground-mounted and roof-mounted systems have higher LCOEs than 10-year systems. This indicates that a key determinant in keeping economical LCOEs is an OPV system’s longevity. It is important to further note that these metrics have factors beyond the control of systems manufacturers of the field. For instance, the energy yield of a PV system is often spurious and highly dependent on the location upon which it is placed.[133]

EPBT and LCOE values are promising for R2R NFA-OPVs due to their improved longevity over PePV systems, their increasing PCEs and reduction in manufacturing costs. Multiple studies have been conducted with regards to the largest cost components of R2R OPVs. Chang et al. conducted a systematic cost analysis of a series of different hypothetical device structures and PePV devices.[134] The key findings of this study found that materials cost in contrast to other associated manufacturing costs make up the largest components of R2R OPVs. Another study conducted by Machui et al. further broke down the cost components of the materials, elucidating the cost breakdown of each material component;[135] 11b. The two key cost components in reducing manufacturing costs of OPV devices are vacuum-deposited metal electrodes and transparent conducting electrodes (TCEs). Figure 11b depicts a typical NFA-OPV device stack indicating the usually vacuum-deposited top electrode and TCE bottom electrode.

Fabrication of top electrodes, usually made out of Au/Ag or evaporated metal, usually requires vacuum deposition and is a highly time-consuming process that requires printed samples to be taken off a line into a metal evaporator or sputterer. Although a robust method of producing high-quality devices, difficulty in patterning, the large amount of time taken, materials used and the necessary environment (e.g., vacuum conditions, etc.) make it a highly unscalable and costly method of fabricating electrodes. Much is to be desired in developing a method to replace these top electrodes such as depositing them via printing/coating. Potential materials that have been investigated include conductive polymers such as PEDOT:PSS,[135] Ag grids made from Ag nanowires or nanoparticles,[31,33,196] and carbon-based compounds such as graphene and CNTs.[164,197–200] However, it must be noted that deposition of such evaporated alternatives using solution-processed electrodes is highly
dependent on the printing/coating method employed. For instance, nondiluted silver nanowire would ideally be deposited using methods that are capable of printing high viscosity solutions (i.e., screen printing). It should also be noted that viscosities and parameters of solution processed electrodes should be engineered in order to facilitate deposition for each chosen deposition method (i.e., highly viscous solutions should be diluted prior to using slot-die for deposition.)

The bottom electrode in most printed PV applications is usually a TCE, traditionally consisting of indium tin oxide (ITO), a highly conductive, transparent but brittle TCE that requires predeposition on a flexible substrate before functional printing. ITO is generally expensive and difficult to pattern with pre-ITO coated rolls usually ordered in bulk. Not only does this affect its flexibility in fabricating custom-shapes, it also adds greatly to the final LCOE of the system. As with vacuum deposited electrodes, many materials have been investigated as potential ITO replacements.

These components hence represent a bottleneck in the drive to reduce the overall EPBT and LCOE of R2R NFA-OPVs. Table 2 consists of a list of potential alternative materials than can be used to replace both vacuum-deposited metal electrodes and TCEs.

### 5.3. Machine-Learning Accelerated Multi-Component R2R NFA-OPVs

One of the big advantages in the use of NFAs is the application of ternary strategies in order to attain ever-improving PCEs.[69] These ternary strategies involve introducing and optimizing a third component into an NFA device which can greatly enhance PCEs in NFA-OPVs.[205–207] Introducing this third component complements or extends the light absorption band of the host device and improves the morphology of the active layer.[18,208,209] Industry-accepted methods such as design of experiments (DoE) have been used in the optimization of components for formulation problems.[200,210,211] They however, generally remain niche tools and require a large number of experiments in order to achieve multi-parameter scanning.

Machine learning strategies have recently gained increasing interest in the materials sciences[212,213] and consequently have been used in donor:acceptor design and optimization for OPVs.[13,189,214,215] Machine learning strategies however require large datasets in order to be effectively utilized. Lopez et al. utilized machine learning from >51 000 NFAs from the Harvard organic photovoltaic dataset,[216] an open-source data set, to identify 838 high-performing molecules (PCE > 8%).[13] In addition, Padula et al. predicted the efficiencies of various donor–acceptor combinations using a machine learning kernel ridge regression model established from published PCEs of 320 organic donor–acceptor pairs.[215]

AI-assisted NFA research is hence, highly multi-dimensional and requires platforms that will be able to gather large amounts of NFA-related data. Often custom, automated data collection rigs have to be designed in order to achieve this. Du et al. was able to achieve a degree of this with a custom-robotic rig which was able to screen 100 processing variations within 70 h.[189] The automated robotic rig reproduced devices reliability. Figure 11d depicts the $J-V$ curves and PCE distribution of 36 solar cells from a single fabrication run from a robotic rig, fabricated using the same parameters with 36 normalized absorption spectra of active-layer films taken in the middle of each solar cell. Reproduced with permission.[189] Copyright 2021, CellPress e) Predicted PCEs of 125 000 deposition parameters created by ML and extracted prediction data to find the performance trend and deposition density (DD) and the f) counts of the number of devices in a 2D composition map. Reproduced with permission.[21] Copyright 2015, Royal Society of Chemistry.
While this is indeed a significant step in the area of dense data collection for NFA-OPV, the optimization of devices produced by Du et al. were based on a single donor:acceptor pair. Scaling beyond two combinations will likely result in more complex engineering issues. Most recently, An et al. demonstrated machine-learning ternary R2R NFA-OPVs with a PM6:Y6:IT-4F photoactive layer on continuously moving substrates. In total, 2218 devices were fabricated and used to train a random forest regression algorithm which produced a model with a 97.7% fit ($R^2 = 0.977$).[21] Using this model, An et al. were able to generate 125,000 different formulations based on fractional components of PM6:Y6:IT-4F and their predicted PCEs; Figure 11e,f. To the knowledge of the authors, this is the closest demonstration to the use of machine learning to generate a predictive model for R2R NFA-OPV design. Models like this can easily be expanded to other ternary (3d) designs and potentially even lead to effective prediction of 4d and even 5d combinations of NFAs for higher breakthroughs of PCE. Machine learning techniques can hence help to either assist or even accelerate the development of R2R NFA-OPVs.

| Alternative material | Electrode | Advantages | Disadvantages | Demonstrated with NFA-OPV | Potential Deposition Methods | Refs. |
|----------------------|------------|------------|---------------|---------------------------|-----------------------------|------|
| Pristine PEDOT:PSS/ conductive polymers | Top/bottom | Rheologically, printable, and easily processable. | Poor transmittance values | No | Slot–die Blade Screen Inkjet | [195] |
| Cu-Ni (sputter-coated) | Bottom | Cheaper than ITO | Requires sputtering Not scalable | No | – | [201] |
| ZTO/Ag/ZTO | Bottom | Improved PCE values from ITO | Requires sputtering three layers likely to be expensive at scale Not easily patternable | No | – | [202] |
| Ag grid+PEDOT:PSS +ZnO | Bottom/top | Good rheological control, excellent morphology, smoothness and printability | Poor transmittance values compared to ITO Complex formulation required | No | Screen Gravure | [33] |
| PEDOT:PSS (with printed silver grids) | Bottom/top | More printable than pure silver dispersions | Requires ink optimisation/ formulation | No | Slot–die Blade Screen Gravure | [33] |
| PEDOT:PSS (With carbon layers) | Top | Significantly (66%) cheaper than metal alternatives Highly flexibility and active area efficiency sustainable | Poor edge seals requiring further encapsulation (possible with conducting polymer) Poor conductivity compared to ITO | No | Slot–die Blade Screen | [199] |
| Carbon nanotubes (CNTs) | Top | Has inherent flexibility Raw material, carbon, is cheap and widely available Easy to solution process Has good preferential hole conduction properties | Very poor transmittance values compared to ITO Difficulty in controlling 1d structures Poor PCE of final device | No | Slot–die Blade Screen Gravure Inkt | [198] |
| Graphene | Top | Single or bi-layer doped graphene can be used as a TCO Theoretical strength and flexibility values are excellent | Potentially expensive at scale (difficult to control layers, flake size and purity) High Rs. Single or bi-layer graphene requires CVD deposition | No | CVD (Mono/bi-layer) | [197] |
| AgNW dispersions (printed as grid) | Bottom/top | Large area deposition possible Easily patternable Maintains good transmission through devices excellent flexibility Highly compatible with wide format systems such as gravure printing Does not require thick layers Rs. can be easily tuned | Junction resistance exists at interface without annealing Important to take ink design into consideration Expensive May cause additional mode of failure by puncturing photoactive layers in devices. | Yes | Spray Screen Gravure Slot–die Blade | [196, 203, 204] |
| Ag anoparticle dispersions (printed as grid) | Bottom/op | Large area deposition possible Highly patternable Compatible with wide format systems such as gravure printing Does not require thick layers Rs. can be easily tuned Maintains good electron transmission through devices | Shadow-loss issues in thick printed areas Achieving smooth substrate topography will require further sintering Junction resistance exists without sintering | Yes | Screen Gravure | [31, 162] |
5.4. Commercialization Efforts of R2R Fabricated OPVs: Past, Present, and Future

In comparison with R2R F-OPVs, commercialization for R2R NFA-OPVs are almost non-existent due to the nascent nature of the materials. However, the commercialization ecosystem for conventional R2R F-OPV systems has undergone significant evolution for a product-market fit and identifying good application areas. It is highly likely that R2R NFA-OPVs will likely take the lead on further commercialization efforts for R2R OPVs moving forward. This section highlights previous, present and future commercial directions that conventional R2R-OPVs and hence likely NFA-OPVs will follow.

5.4.1. The Past: A Failure to Replace Conventional Si-PVs

The early 2000s marked the era when OPV technologies was viewed as a commercially viable alternative PV technology to Si-based solar cells [218,219]. A pioneer company, Konarka (established 2001), was the first company to attempt large-scale commercialization of OPVs as a spin off from the University of Massachusetts Lowell. Konarka attained a moderate level of success, attracting ≈USD $200M of investment, thereby enabling them to achieve large scale production; Figure 12a. Among their achievements was a fully functional fabrication plant with a 1 GW per year production capacity based on 5% PCE of modules.[18] Figure 12a depicts a solar-powered bag with an integrated printed OPV module fabricated by Konarka’s facility. Konarka established themselves as the global leader of the commercialized R2R OPVs technology and reported many record-breaking efficiencies of OPVs. However, the PCEs of the company’s commercialized R2R printed modules plateaued at 3% PCE[220] until its bankruptcy in 2012. A post-mortem of the bankruptcy of Konarka was generally attributed to a number of reasons that made R2R fabricated OPVs a poor PV alternative to conventional Si technologies. The inability to achieve higher PCEs due to the intrinsic material limitations of F-OPVs keeping the overall LCOE high and unattractive to funders. In addition, the dramatic decline in prices of crystalline Si PV from $3 per Watt-peak(Wp) to <$1 per Wp[221] made competition stiffer for Konarka’s final product. As a result, Konarka was unable to identify a “killer application” that took advantage of the flexible, lightweight, colorful and semi-transparent PVs that they fabricated.

5.4.2. The Present: Finding Niche Applications

Successors of Konarka (companies such as Belectric OPV, OPVIUS, and currently ARMOR) have been making a significant efforts on differentiating their OPVs from other PV technologies. Figure 12c depict an example of OPV deployment in a distinctive way by Belectric OPV (OPVIUS). The company fabricated a unique hexagonal module (Figure 12c inset) to match the architectural design of the structure. This unique and flexible design, unachievable by conventional Si-PV, is the product of the company’s innovation efforts that vastly enhances the applicability of R2R fabricated OPVs and demonstrated various attractive products/demonstrators, including OPV integrated cars, street furniture, and building façades.[222] InfinityPV, a spin-off from DTU established by Krebs and coworkers, is another OPV company that produced innovative OPV products. The company has developed an innovative module design, called infinity PV, that allows infinite number of series connections during the R2R manufacturing process and can be cut-to-size for various scale applications.[223] The module was used to demonstrate a significant 100 m module with over 10 000V of operating voltage. One drawback of the design was in the wiring of these lengthy modules. This was overcome by a further development of a bidirectional module; Figure 12d, which allows more practical single power point extraction. Other commercial OPV products the InfinityPV team has produced include a retractable OPV-powered USB charger which demonstrate various competitive advantages of R2R fabricated OPVs; Figure 12e.

A research team at the Commonwealth Scientific and Industrial Research Organization (CSIRO), the national science agency of Australia, has also been actively developing R2R fabrication technologies for OPVs with a commercialization objective. While most OPV modules are characterized by long stripes due to the use of slot-die or flood-coating technologies, the team developed a stripe-free module design, analogous to ARMOR’s module, that requires no expensive laser processing. This design allows embedding simple images or logos, as shown in Figure 12f, which would add value to commercial OPV products. The team also developed a smart module design, as shown in Figure 12h, with a configurable series and parallel connections for controlled voltage output. The design mitigates practicality issues with regard to the uncontrolled high voltage of infinity PV design. The versatility of such a module is used in a demonstration solar canopy, as shown in Figure 12i, with commonly available 48 V inverters. A multitude of other R2R-fabricated OPV companies are also active in the space that have produced equally interesting demonstrator applications. Sunew demonstrated the world’s largest OPV-based building-integrated PV (BIPV) with 1000 m² of laminated OPV glasses.[223] OE-Technologies, demonstrated various OPV demonstrators integrated with buildings, structures, and furniture.[224]

A brief commercial survey of present day industry activity has shown multiple companies active in the space of R2R-fabricated OPV commercialization, thereby lending credence to the commercial resurgence of OPVs and the new renaissance of NFA-OPVs. Despite early failures in commercialization efforts by Konarka, these new companies are finding niche applications and carving a unique space in the PV market. Overall, the prospects for R2R fabricated OPV look bullish and will likely be a disruptive force in the human existence in time to come. However, it must be noted that OPV technology has yet to penetrate daily life and the continuous development of innovative ideas on OPV-deployment must be developed concurrently while improving efficiencies of OPV devices using NFAs.

5.4.3. The Future: BIPVs, Space, IoTs, and Beyond.

While the present day ecosystem remains active, it is important to establish future missions and high-value markets that allow
the sustainable growth of OPV fabrication. The rapid decrease in price of Si PV make it difficult for R2R fabricated OPV technologies to effectively compete with the secure economies of scale of its incumbent. This is especially so in the mass power market. As such, it is important to identify other application areas of R2R fabricated OPVs that will be able to take distinct advantages of R2R OPVs semi-transparency, lightweightness and flexibility. 

**Figure 13a** depicts a graph of niche PV markets that are smaller than the general on-grid power market with significantly higher energy prices and requirements for the application. 

Aerospace applications, a rapidly expanding and highly premium market, has a strong fit for lightweight R2R OPV films. The rapid growth of the space sector in recent years has seen a marked increase in the demand for PVs for space applications which is not as price sensitive as conventional power grids. At present, space applications with their increased tolerances for higher power generation prices ($100–200 per Wp)$\textsuperscript{[1]} is a highly attractive industry space for R2R fabricated OPVs. Figure 13b depicts OPV devices developed for space applications. Simulation work done on such devices has shown that OPVs can survive in the harsh and highly radioactive space environment without significant PCE loss; \textsuperscript{[226,229]} The space application market is currently dominated by high-cost and high-efficiency multi-junction PV devices due to the limited PV installation areas. Flexible, rollable, and lightweight OPV films would be able to expand the light-harvesting area if the films are prepared as shown in and unrolled in the space and compensate efficiency difference.

BIPVs are one of the high-value market sectors that R2R fabricated PVs have a distinct advantage over conventional Si-PVs,
leading to many present day industry players pursuing applications in the sector. A subset of this highly promising area is indoor applications. OPV devices have shown over 30% PCE under indoor light\cite{190} and superior performance than Si-PVs under low lighting conditions; Figure 13d. With the boom of the internet of things (IoTs), there have been increasing demands on the integrated power source of IoTs and other low-power electronics. As shown in Figure 13e, OPVs would be able to power small electronics as an energy-harvesting device for indoor light energy. OPV films can be fabricated on an extremely thin substrate allowing high power-per-weight, extreme flexibility and even stretchability; Figure 13f. Such features also make OPVs suitable for an integrated power source of wearable biomedical devices; Figure 13g,h. These emerging markets together with the rapidly increasing PCEs of NFA-OPVs have meant a new resurgence for the commercial use cases for OPV technology.

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Conflict of Interest
The authors declare no conflict of interest.

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