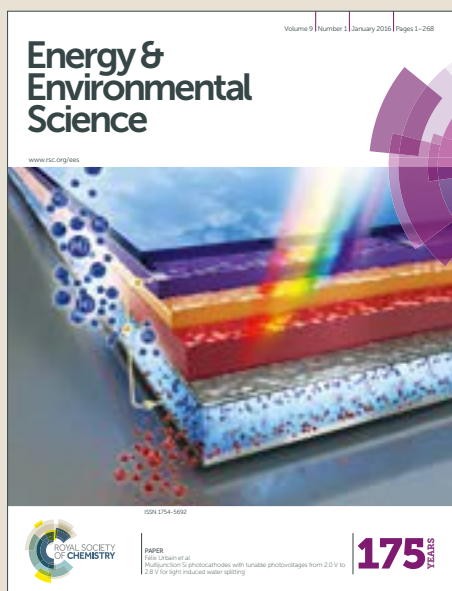


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Analyzing the efficiency, stability and cost potential for fullerene-free organic photovoltaics in one Figure of Merit

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Abstract

The power conversion efficiencies (PCEs) of solution-processed organic photovoltaics (OPV) devices continue increasing towards the 15% milestone. The recently-emerging non-fullerene acceptors (NFAs) have significantly accelerated this development. Most of the efficiency analyses performed previously are based on a fullerene acceptor without considering its contribution to the enhancement of photo-absorption and PCE. Moreover, the stability and cost potential of OPV devices are usually not discussed, which sometimes makes the efficiency prediction less representative for broad interest. In this work, we effectively combine the prediction of efficiencies with experimentally determined stability data to analyze and predict the commercial potential of a NFA-based OPV product. Assuming that NFAs dominate the blend near IR absorption, the efficiency limit of OPV devices is predicted to be close to 20% and is found to be insensitive to the donor bandgap. Along with the excellent photo-stability observed for state-of-the-art NFA-based OPV devices, it is suggested to design corresponding customized donors with promising processing properties, excellent environmental stability and low synthesis complexity as a realistic material pair for large-scale production and commercialization.

Broader context

The success of a photovoltaic technology is determined by an optimal combination of efficiency, lifetime and production cost. It is generally accepted that a module efficiency of >10% in combination with an operational lifetime of >10 years and a production cost of $\ll 1\text{€}/\text{W}_{\text{peak}}$ is suggested for industrial production of organic solar cells (OSCs). Great progress has been made over the last years in developing highly efficient and stable OSCs with device performance exceeding 12%. The recently-emerging non-fullerene acceptors have significantly accelerated this progress and boost the performance of OSCs towards the 15% milestone. However, apart from the performance and stability, the production cost, especially the materials cost, plays an essential role in determining the success and industrial viability of OSCs. In this analysis, we step-by-step analyze the efficiency, stability and cost potential for OSCs in one Figure of Merit, which allows us to directly compare the industrial viability of OSCs based on various material systems. Moreover, the analysis clearly suggests that organic semiconductors with low synthetic complexity, such as P3HT, would be the preferred choice for large-scale production and commercialization, if a promising and compatible acceptor is available.

1. Introduction

After two decades of rapid development, organic photovoltaics (OPV) technologies have reached a respectable scientific level of understanding with excellent power conversion efficiencies (PCEs) of over 13% for solution-processed lab-scale devices, approaching a tipping point for large-scale production and commercialization.¹⁻⁸ The advantages of OPV devices, such as light weight, semi-transparency, low cost and easy manufacturing on large-scale, make OPV a very attractive technology for non-grid connected applications.⁹ To further stimulate market growth of the OPV technology, its potential has to be analyzed in terms of efficiency, stability and cost, in particular for the recently emerging non-fullerene acceptors (NFAs).

Solution-processed fullerene derivatives, such as phenyl-C₆₁-butyric acid methyl ester (PCBM), have been predominately used as the acceptor in bulk-heterojunction (BHJ) organic solar cells (OSCs) since mid-1990s, boosting the efficiency of OSCs to the 10-12% regime.¹⁰⁻¹⁸ However, fullerene-based acceptors have some inherent disadvantages, such as low absorption in the abundant regions of the solar spectrum and a low miscibility with most conjugated polymers resulting in strong agglomeration upon thermal stress, which has been delaying market development for OPV. NFAs have emerged during the last 5 years as a promising alternative to fullerenes.^{19, 20} Great effort has been devoted to developing NFAs with tunable optoelectronic properties and promising stability.¹⁹⁻³² The champion efficiency of over 13% was obtained by combined molecular optimization of both polymer donor and non-fullerene acceptor, respectively.² Moreover, excellent thermal stability and device stability under illumination were reported for OSCs based on NFAs, indicating significant potential for commercialization.^{33, 34} The recent progress in developing non-fullerene acceptors for OSCs has been summarized in several review papers.¹⁹⁻²³

Although a huge number of OPV donors and acceptors have been developed in the last decade, boosting the efficiency up to 13%, the processing properties of state-of-the-art OPV materials under ambient conditions using a roll-to-roll compatible printing method still remain a challenge. This is mainly due to the insufficient environmental stability of OPV materials as well as the delicate BHJ micromorphology that is required to optimize charge carrier generation and transport.^{35, 36} It is accepted that the success of a PV technology is determined by an optimal combination of efficiency, lifetime and production cost. To push the PV technology towards commercialization, a module efficiency of >10% in combination with an operational lifetime of >10 years and a production cost of $\ll 1\text{€}/W_{\text{peak}}$ is required.⁹ OPV technology has unique properties compared to other commercial PV technologies, such as flexibility, semi-transparency and colorful device configurations, and as a result, OPV devices may find application in niche products which require moderate requirements in terms of module efficiency, operational lifetime and production costs for mobile or de-centralized applications in daily life. Therefore, the OPV design rules for a successful mass product are distinctly different from roof-top or green-field grid-connected PV technologies renewable power stations.⁹

In our previous work, an industrial figure of merit (i-FoM) was introduced for solution-processed OSCs based on molecular donors and PCBM as acceptor.³⁷ Three essential factors, namely efficiency, stability and cost of materials, were taken into account to assess the industrial product interest. The definition of the i-FoM is given by:

$$i - FoM = \frac{PCE \times \text{photostability}}{\text{synthetic complexity}}$$

More than 30 molecular donors were analyzed in combination with PCBM, and the i-FoM value was found to vary between 0.05 and 0.15.³⁷ Based on experimental results and simulation data, an i-FoM value of 0.2 along with a PCE of > 14% was found at that stage as a benchmark for

industrial production. However, a PCE of >14% is already at the efficiency limits of single-junction OPV devices based on PCBM as acceptor according to Scharber et al.³⁸⁻⁴⁰ It was challenging to simultaneously develop material combinations satisfying high efficiency, long-term stability and a cost-efficient synthesis, and nearly all synthetic efforts are concentrated on achieving high efficiencies instead. Nevertheless, the quickly emerging NFAs offer the potential to address these three challenges in parallel, as the recent progress showed high efficiencies and lifetimes in parallel. The molecular acceptors are developed on the one hand to broaden the absorption of OSCs, and on the other hand to increase the open-circuit voltage (V_{OC}) by minimizing the lowest unoccupied molecular orbital (LUMO) level difference between donor and acceptor. A remarkable short-circuit current density (J_{SC}) of >25 mA cm⁻², an unprecedentedly low non-radiative V_{OC} loss of 0.20 V and an excellent fill factor (FF) of >75% have been demonstrated in individual NFA-based OPV devices, exhibiting serious scientific potential to develop the efficiency of OSCs beyond the currently predicted single-junction limit of about 15%.⁴¹⁻⁴³

In this work, we adopt the i-FoM approach to analyze the efficiency, stability and product relevance of NFA-based OSCs according to combined experimental results and simulation data. Three model polymers are used as donors, while PCBM and one recently developed NFA are used as acceptors for the i-FoM analysis. The comparison to PCBM is included to highlight the difference in general design rules for these two material generations. According to the recent findings on efficient charge dissociation at donor: acceptor interfaces with minimized energy difference, we reformulate conditions defined for theoretical efficiency prediction, and find that an excellent efficiency of ~20% can be achieved for the three donor materials when an “ideal” acceptor is used. Moreover, a stable BHJ morphology and device stability can be expected for

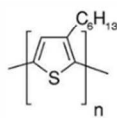
NFA-based OPV devices. Therefore, the value of *i*-FoM is only determined by the synthetic complexity (SC) of the donor and acceptor materials. Interestingly, OPV materials with simple chemical structures and synthetic routes, such as poly(3-hexylthiophen-2,5-diyl) (P3HT), will be ultimately the most promising candidates for large-scale production and commercialization.

2. Results and Discussion

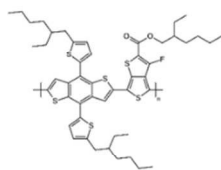
The chemical structures of three model polymers, P3HT, Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2,6-diyl)] (PCE10 or PTB7-Th) and Poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3''-di(2-octyldodecyl)-2,2';5',2'';5'',2'''-quaterthiophen-5,5'''-diyl)] (PCE11 or PffBT4T-2OD) are illustrated in Figure 1. The three polymer donors were chosen owing to their excellent performance in combination with the chosen NFA and stability when printed under ambient conditions.^{35, 44, 45} The SC index of the three polymers and the two acceptors were estimated according to Po et al.,⁴⁶ summarized in Table S1, while their efficiencies and stabilities were taken from literature, summarized in Table S2.^{44, 47, 48} It is worth mentioning that the efficiency data were taken exclusively from literature reports where corresponding stability data are available, which significantly limits the available data. Moreover, we are aware that it's difficult to unify standards for estimating the SC values of different materials, especially the fullerene-based acceptors. However, even for the same materials the synthetic routes described by different research groups may result in slightly different SC values. Nevertheless, the slightly different SC values do not affect the discussion and conclusion of this analysis work. Different from the previous *i*-FoM analysis, the SC index of acceptor was also taken into account in this study by defining the SC index of the BHJ

mixture (SC index (M)), where the polymer and the acceptor index are averaged according to the weight ratios used (Table S3).

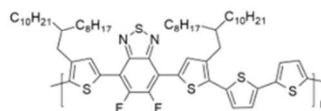
In a first step, the i-FoM values were calculated for the three polymers blended with PCBM by adopting the experimental results and the estimated SC index (M), as summarized in **Table 1**. The calculated i-FoM values range from 0.183 for P3HT: PCBM, and 0.229 for PCE10: PCBM to 0.258 for PCE11:PCBM. As defined by Po et al., the SC index scales differently for polymers and molecular donors.⁴⁶ Therefore, the absolute values of the i-FoM calculation cannot be directly compared with our previous analysis on molecular donors. Nevertheless, the analysis made for this study followed identical boundary conditions, and therefore allows to directly compare the different donors as well as the different acceptors. Although P3HT exhibits the lowest of all efficiencies with only 2.8%, the extremely low SC index of 7.7% (14.1% for the P3HT: PCBM 1:1 mixture) and the good stability factor of 0.92 make it surprisingly attractive compared to other high-performance state-of-the-art donors for industrial production. The i-FoM values were estimated to be 0.229 for PCE10: PCBM and 0.258 for PCE11: PCBM, which were mainly limited by the high SC index of PCE10 (64.3%) and the strong burn-in degradation of PCE11:PCBM (200 hrs stability = 0.67).

Donors

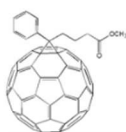
P3HT



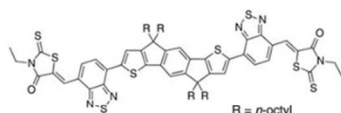
PCE10



PCE11

Acceptors

PCBM



O-IDTBR

Figure 1. Chemical structures of donors and acceptors investigated in this study.

By replacing PCBM with the NFA O-IDTBR, the *i*-FoM values of all combinations increased significantly due to either improved PCE or enhanced stability values. For instance, the PCE is improved from 2.8% for P3HT: PCBM to 6.05% for P3HT: O-IDTBR. No degradation was observed for PCE11: O-IDTBR solar cells, while the PCE11: PCBM solar cells suffered from a noticeable burn-in degradation. However, due to the high SC index of O-IDTBR (43.9%), the SC index of BHJ mixtures with NFAs was estimated to be higher than that with PCBM mixtures. Overall, the *i*-FoM value was slightly improved from 0.183 for P3HT: PCBM to 0.230 for P3HT: O-IDTBR, while PCE10: O-IDTBR and PCE11: O-IDTBR exhibited almost unchanged *i*-FoM of 0.219 and 0.255, respectively. Although a remarkably high PCE of 12% and an excellent device stability was attained for PCE10: O-IDTBR, the much more complex synthesis of PCE10 and O-IDTBR limits the SC index to 52.1%. Nevertheless, it is notable that all the polymer: O-IDTBR blends exhibit excellent device stability, which contributes to satisfying the lifetime requirement for commercial applications.

By employing NFA acceptors in BHJ blends, both J_{SC} and V_{OC} of OPV devices can be

simultaneously improved compared to the PCBM-based control devices. As already mentioned above, the improved J_{SC} is related to the broadened optical absorption contribution from the NFAs, while the improved V_{OC} originates from the optimized energy level difference.^{24, 29} Moreover, recent publications reported that the charge transfer states of NFA-based PV devices were either not identified at all, or found to be much higher than that of corresponding PCBM-based devices, which is also beneficial to an enhanced V_{OC} .^{42, 49} It seems that the difference in highest occupied molecular orbital (HOMO) level between donor and NFA is not critical for efficient charge dissociation. Several groups reported that a minimized HOMO level difference less than 0.1 eV in solution-processed OPV device could still deliver EQE values > 0.6 .^{43, 50-52} In the next step, we will introduce an improved model to predict the efficiency limit for NFA-based OSCs. The model used by Scharber et al., as illustrated in Figure 2a, is solely based on the PCBM acceptor, and the absorption of PCBM is not considered for efficiency prediction.^{38, 39} The LUMO level of PCBM (E_{LUMO_PCBM}) is fixed at -4.0 eV, and the V_{OC} is defined by the energy difference between the E_{LUMO_PCBM} and the HOMO of donor (E_{HOMO_Donor}) with an additional energy loss of 0.3 eV. The LUMO of donor (E_{LUMO_Donor}) is defined to be higher than the E_{LUMO_PCBM} with a smallest energy difference of 0.3 eV empirically assumed for efficient charge dissociation, corresponding to bandgap-to- V_{OC} loss of 0.6 V. The J_{SC} is determined by the bandgap of donor (E_{g_Donor}) with an assumed constant external quantum efficiency (EQE). Along with a constant FF, the PCEs are therefore predicted as a function of the E_{g_Donor} and the LUMO difference between donor and PCBM.

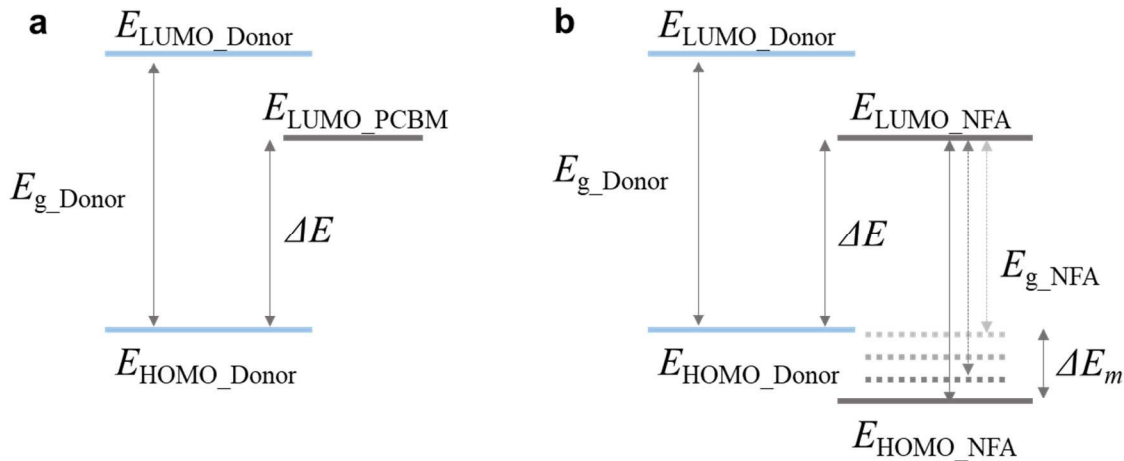


Figure 2. Energy levels of a donor and an acceptor used for predicting the efficiency of OPV devices based on PCBM (a) and NFAs (b).

Figure 2b describes the modified model used in this study, which takes the absorption of NFAs better into account. It is defined in the model that the $E_{\text{LUMO_Donor}}$ and $E_{\text{HOMO_Donor}}$ are always higher than the $E_{\text{LUMO_NFA}}$ and $E_{\text{HOMO_NFA}}$, respectively, without defining a smallest energy difference. Owing to the gradual absorption onset, bandgap fluctuations, non-ideal charge carrier collection efficiency and additional non-radiative recombination, the V_{OC} of OSCs is much lower than the value determined by the detailed balance limit ($V_{\text{OC,SQ}}$).^{53,54} The V_{OC} of OSCs is therefore given by:

$$V_{\text{OC}} = E_g/q - \Delta V_{\text{OC,SQ}} - \Delta V_{\text{OC,rad}} - \Delta V_{\text{OC,nr}} \quad (1)$$

where E_g is the smallest bandgap of either donor or acceptor, q is the elementary charge, $\Delta V_{\text{OC,SQ}}$ is the loss defined by the Shockley-Queisser theory, $\Delta V_{\text{OC,rad}}$ is the additional loss related to radiative recombination and the $\Delta V_{\text{OC,nr}}$ is the loss due to non-radiative recombination. The $\Delta V_{\text{OC,SQ}}$ is typically between 0.25 and 0.3 V for a semiconductor with bandgap between 1.2 and 2 eV. $\Delta V_{\text{OC,rad}}$ can be as low as zero, while a remarkably low $\Delta V_{\text{OC,nr}}$ of 0.2 V was observed for OSCs.⁴³ To simplify the efficiency calculation, we define a bandgap-to- V_{OC} loss ($\Delta V_{\text{OC,Eg}}$) of

0.45-0.5 V as a rational limit for OSCs. By taking into consideration the energetic mismatch between $E_{\text{HOMO_Donor}}$ and $E_{\text{HOMO_NFA}}$ (if $E_{\text{g_Donor}} \geq E_{\text{g_NFA}}$) or between $E_{\text{LUMO_Donor}}$ and $E_{\text{LUMO_NFA}}$ (if $E_{\text{g_Donor}} \leq E_{\text{g_NFA}}$), the V_{OC} of OSCs is described as

$$V_{\text{OC}} = E_{\text{g}}/q - \Delta V_{\text{OC,m}} - \Delta V_{\text{OC,Eg}} = \Delta E/q - \Delta V_{\text{OC,Eg}} \quad (2)$$

where $\Delta V_{\text{OC,m}}$ is the energetic mismatch, $\Delta V_{\text{OC,Eg}}$ is the bandgap-to- V_{OC} loss (0.45-0.5V for OSCs) and ΔE is the energetic difference between $E_{\text{HOMO_Donor}}$ and $E_{\text{LUMO_NFA}}$. Since both donor and acceptor contribute to the absorption of photons and the generation of photocurrent, we simplified the J_{SC} calculation by only using the smallest bandgap estimated for donor and acceptor, as illustrated in Figure S1. Under the assumption of a constant EQE = 0.8, a FF = 0.75 and a $\Delta V_{\text{OC,Eg}} = 0.5$ V, the efficiencies of the three model polymers are calculated and plotted as a function of the $E_{\text{g_NFA}}$ as well as the $E_{\text{LUMO_NFA}}$ in Figure 3. The optoelectronic properties of the three polymers, including energy levels, electrical and optical bandgaps, etc. are taken from literature and summarized in Table S4.^{3,29} The electrical bandgaps, estimated by the energy difference between HOMO and LUMO, are in good agreement with the corresponding optical bandgaps determined by the absorption of thin films. Although the bandgaps of the three polymer donors range from 1.9 to 1.6 eV, the highest achievable PCEs of 17.6% are of course identical for all polymers as an ideal non-fullerene acceptor (i-NFAs) with a bandgap of ~1.4 eV dominates absorption as well as the J_{SC} of OSCs. The highest PCEs are achieved for an i-NFA with a bandgap of ~1.4 eV and a HOMO level being equal to that of the polymer donor, i.e. $\Delta V_{\text{OC,m}} = 0$. In this case, the LUMO level of i-NFA has to be correspondingly adjusted for given organic donors to reach the highest possible efficiency.

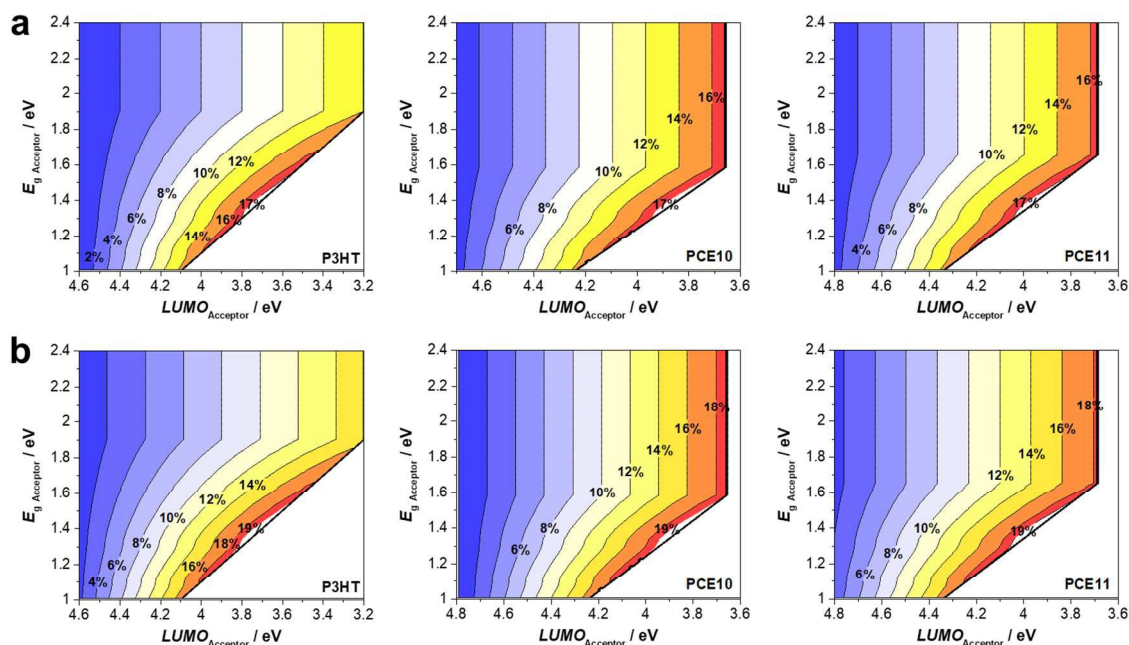


Figure 3. Prediction of PCEs of single-junction OPV devices based on P3HT, PCE10 and PCE11 by taking into account the contribution of NFAs. The prediction was performed based on the improved model described in Figure 2b under the assumptions of (a) a bandgap to V_{OC} loss = 0.5 V, a constant EQE = 0.8 and a FF = 0.75; (b) a bandgap to V_{OC} loss = 0.45 V, a constant EQE = 0.8 and a FF = 0.8.

The efficiency was again calculated under the assumption of a constant EQE = 0.8, a FF = 0.8 and a $\Delta V_{OC,Eg} = 0.45$ V, in which case the highest achievable PCEs were enhanced to 19.8% for all the three polymers. These assumed values are still reasonable by comparing with the values used in literature for efficiency calculation, and the highest values reported for OSCs.^{2,3,39,40} As depicted in Figure 3, the optimal bandgap of i-NFAs still remained at ~ 1.4 eV. For both cases, the V_{OC} loss is only related to the E_{g_NFA} with a $\Delta V_{OC,Eg}$ of 0.5 or 0.45 V. According to the Shockley-Queisser limit, a V_{OC_SQ} of 1.14 V is determined for a semiconductor with a bandgap of 1.4 eV, corresponding to a $\Delta V_{OC,SQ}$ of 0.26 eV.⁵³ The assumed $\Delta V_{OC,Eg}$ of 0.5 or 0.45 V is reasonable for achieving the highest possible PCE of 17.6% or 19.8%, which is rationally higher than the efficiency predicted for PCBM-based OSCs.³⁹ It is worth mentioning that a constant EQE of 0.8, a FF of 0.8 and a low bandgap-to- V_{OC} loss of 0.45 V might not be feasible for every OPV

system. Nevertheless, based on the very promising experimental values reported for state-of-the-art OSCs, we are quite optimistic that OPV technologies have the great potential to reach the suggested efficiency limit of 19.8%.

In this work we take the PCE of 19.8% for calculating the i-FoM values of OSCs based on i-NFAs. By taking the stability value of 1.00 (PCE11:O-IDTBR) and attributing the SC index of i-NFA to be the same as PCBM, the i-FoM values are re-calculated for polymer: i-NFA blends and summarized in Table 1. As the PCE and the stability are the same for all the combinations, the i-FoM is only determined by the SC index of the donor and acceptor. Not surprisingly, owing to its smallest SC index, P3HT emerges as the most attractive donor in combination with i-NFA in terms of industrial interest and commerciality. The very impressive i-FoM of 1.404 for P3HT: i-NFA, which is six times higher than that of PCBM- and O-IDTBR-based OPV devices, will be a benchmark for evaluating the commercial potential of next-generation OPV materials in terms of efficiency, stability and cost. It is worthwhile to underline again that the i-NFA is proposed to explore the highest possible i-FoM for the three model polymers under the assumption of excellent device performance and stability. It is very interesting to know that the device performance is no longer determined by the polymer donors, but the optoelectronic property of the i-NFA. Back to the discussion on the requirements for industrial viability, a module efficiency of >10% in combination with an operational lifetime of >10 years and a production cost \ll 1€/W_{peak} is required. The most critical point here is the production cost. The P3HT:PCBM system, which gives a SC index of 14.1%, would be the cheapest material combination so far. By taking the SC of 14.1% along with a device stability of 98% and a PCE of 10%, an i-FoM value of \sim 0.7 is obtained, which can be considered as a benchmark value for industrial production of OSCs. By taking into consideration the suggested benchmark i-FoM

value of 0.7, the equation describing the industrial viability of OSCs is therefore given by

$$\frac{PCE \times \text{photostability}}{\text{synthetic complexity}} \geq 0.7$$

The selection of material combinations is more relaxed for OSCs with high PCE. By taking the stability of 100% and the highest possible PCE of 19.8% predicted for OSCs based on i-NFA, the corresponding SC value is calculated to be ~28%. For OSCs with efficiency lower than 19.8%, a corresponding low SC (limited materials) has to be taken into consideration for commercialization. We may therefore conclude that any material system that has a SC index larger than 28% (for instance PCE10-based OSCs) cannot reach an i-FoM value of 0.7, which is nearly impossible for industrial production.

Table 1. Parameters used for estimating the i-FoM of OPV devices based on the four model polymers blended with different acceptors. ^{a)} Unpublished measurement data.

	PCE / %	200 hrs Stability	SC index (M) / %	i-FoM	Ref.
Blended with PCBM					
P3HT	2.8	0.92	14.1	0.183	⁴⁷
PCE10	8.87	0.91	35.2	0.229	⁴⁸
PCE11	9.2	0.67	23.9	0.258	⁴⁴
Blended with O-IDTBR					
P3HT	6.05	0.98	25.8	0.230	³³
PCE10	12.0	0.95	52.1	0.219	^a
PCE11	9.5	1.00	37.2	0.255	³⁴
Blended with i-NFA					
P3HT	19.8	1.00	14.1	1.404	-
PCE10	19.8	1.00	35.2	0.563	-
PCE11	19.8	1.00	23.9	0.828	-

3. Conclusion

In this work we analyzed an improved simulation model of efficiency prediction by taking into account the contribution of acceptor to predict the efficiency limit of OPV devices. The simple, semi-empirical model describes the efficiencies of PCBM-based OSCs, and is also valid to

predict the efficiency limit for OPV employing NFAs. We step-by-step analyzed the i-FoM values for three model polymers blended with three acceptors, PCBM, O-IDTBR and a conceived i-NFA that matches the requirement to get the highest possible PV performance. In contrast to the previous models where the contribution from PCBM is ignored, by taking into consideration the absorption as well as the well aligned energy levels of NFAs, a theoretical efficiency limit of 19.8% is predicted as for all the polymer donors investigated with bandgaps ranging from 1.6 to 1.9 eV when blended with a NFA with a bandgap of ~ 1.4 eV. Most importantly, the improved model suggests that the absorption of OPV devices and the bandgap-to- V_{OC} loss will be more relevant to the small bandgap acceptors rather than donors. In such cases, donors with promising processing properties, excellent environmental stability and low SC index, such as P3HT, will be the preferred choice for large-scale production and commercialization. We believe that the simulation model described in this work along with the interesting outcome of efficiency prediction and i-FoM is helpful to the research community to better direct the synthetic efforts for designing novel NFAs for next-generation OPV materials.

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(project EXC 315) (Bridge Funding).

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