Progress in poly (3-hexylthiophene) organic solar cells and the influence of its molecular weight on device performance


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Poly (3-hexylthiophene) was an early frontrunner in the development of donor polymers to be used in organic photovoltaics. A relatively straightforward and inexpensive synthesis suggests that it may be the most viable donor polymer to use in large-scale commercial organic solar cells. Replacing fullerenes with new electron acceptors has led to significant improvements in device performance and stability, with devices now able to exceed an efficiency of 7%. Past studies have reported a dependence of device performance on the molecular weight of the polymer in fullerene-containing blends, however, with nonfullerene acceptors now showing promise a similar study was needed. P3HT blends, with two nonfullerene acceptors (O-IDTBR and EH-IDTBR), were probed using a number of polymer batches with varying molecular weights. O-IDTBR was shown to exhibit a dependence on the polymer molecular weight, with optimal performance achieved with a 34 kDa polymer, whilst EH-IDTBR displayed an independence in performance with varying polymer molecular weight. Probing the thermal and morphological behavior of the P3HT:O-IDTBR blends suggest an optimal morphology, with pronounced donor and acceptor domains was only achieved in with the 34 kDa polymer, and a greater degree of mixing was exhibited in the other blends, likely leading to poorer device performance.

1. **Introduction**

Since their inception over twenty years ago, organic solar cells (OSCs) have progressed from single component layers of organic semiconducting materials to highly tuned, multiple component blends. This added complexity in the design of devices has been mirrored by the increasing complexity of the organic semiconductors used, where rational design has
allowed fine tuning of morphological and optoelectronic properties of the active layer blend, and has resulted in power conversion efficiencies (PCEs) of over 10% to now become commonplace.\cite{1-4} The most popular strategy that has been employed is the use of a bulk heterojunction, in which an electron donor polymer is paired with a small molecule electron acceptor. Until recently, fullerene based electron acceptors, such as phenyl-C$_{61}$ butyric acid methyl ester (PC$_{61}$BM), had been dominant in the field of OSCs; owing to their exceptional electron accepting and transport properties, in addition to their ability to form domains on the scale of the exciton diffusion length (~10 nm in organic semiconductors) when blended with donor polymers.\cite{5,6} However, fullerene-containing devices have not been able to exceed a PCE of 7% with the early wide bandgap donor polymers developed for OSCs, such as poly (3-hexylthiophene) (P3HT), poly (2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and polyfluorenes, though PCEs are often much lower than the record value.\cite{7-9}

This can be traced back to a number of drawbacks that fullerene containing blends possess; (i) the weak absorption of visible light exhibited by fullerenes, which hampers the active layer’s ability to efficiently harvest photons in the visible region of the solar spectrum, (ii) the deep lying lowest unoccupied molecular orbital (LUMO) of fullerenes, which limit the voltage an OSC can achieve and (iii) the long-term morphological instability of fullerenes in polymer blends, resulting in device failure within a matter of days.\cite{10,11}

The poor optical properties of fullerenes were mitigated, more recently, by the use of donor polymers, which were tuned to absorb in more abundant regions of the solar spectrum. The push-pull hybridization, which occurs in donor-acceptor copolymers, was utilized in order to create narrow bandgap materials that were able to compensate for the lack of visible light absorption by fullerenes. This strategy, along with further tuning of the structural properties of the donor polymers to form optimal blend morphologies, led to great strides in improving the performance of OSCs, culminating in the achievement of PCEs as high as 11%.\cite{1,2} Despite this success, the added synthetic complexity of the donor polymers required
to produce such device performance render them incompatible with the large-scale industrialization of OSCs.\textsuperscript{[12,13]} The complex synthesis and high costs that are associated with the production of a number of successful donor polymers, such as PTB7-Th and PffBT4T-2OD, limit the scale on which they can currently be produced in gram quantities, rather than the tonnes required for large scale commercialization. This can be attributed to the need to produce multiple different monomer units, many of which require a number of synthetic steps, along with the need for expensive Pd-catalyzed cross-couplings in the polymerization.

More recently, nonfullerene acceptors (NFAs) have been developed to replace the traditionally favored PC\textsubscript{61}BM, and its analogues. The main principle behind their design was to maintain the favorable electron accepting and charge transport properties of fullerenes, whilst also improving the $V_{OC}$ that can be achieved in devices, through the development of materials with higher lying LUMOs. Additionally, improved visible light absorption and reduced aggregation tendencies of the acceptors was preferable to maximize the performance in devices. Early attempts included acceptors such as subphthalocyanines, truxenones and perylene diimides, which made use of extended fused-ring core units. The extended conjugation of such systems afforded the medium to low bandgaps needed to improve photon harvesting, however an adverse effect of the extended, planar structure of these small molecules was micrometer scale aggregation when blended with donor polymers.\textsuperscript{[14,15]} Additional problems with the processability of subphthalocyanines has led to a significant drop in interest in such systems in the context of organic photovoltaics. Twisted perylene diimide dimers, trimers and tetramers have managed to address the issue of excessive aggregation in blends, yielding a number of promising results, including some of the first examples in which NFAs were able to outperform the analogous fullerene-containing device.\textsuperscript{[16-18]} Additionally, the emergence of acceptor-donor-acceptor (A-D-A) NFAs has led to great progress in the field of OSCs in recent times. These acceptors consist of an electron rich core flanked by electron deficient peripheral units; making use of push-pull hybridization
to create low bandgap materials with high absorption coefficients, without the need for such large planar units in most cases. Another benefit of these acceptors is the ease with which their frontier molecular orbitals (FMOs) can be tuned by varying the strength or electron-rich core, the electron-poor peripheral units, or the inclusion of electron withdrawing (or donating) functional groups. This allows the A-D-A acceptors to achieve exceptional open circuit voltage (V_{OC}) in devices. The donor polymers most commonly used with both perylene diimide and A-D-A acceptors are medium or low bandgap polymers such as PTB7-Th, PffBT4T-2OD and PBDB-T. Although the pairing of NFAs with these complex push-pull copolymers has yielded record breaking OSCs, with several examples of 11-13% PCEs being achieved, the large-scale viability of such acceptors is a significant hurdle.[3,4,19,20]

To date, P3HT remains among the only donor polymers that is suitable for the large-scale commercialization of OSCs, due to its relatively straightforward synthesis and availability of monomer. P3HT is a wide bandgap donor homopolymer (1.9 eV) that consists of a repeating alkylated thiophene monomer unit. The planar nature of thiophene-thiophene linkages renders P3HT a relatively crystalline polymer with extended \pi-electron delocalization along its backbone, as such it has been shown to have good charge transport properties and is often able to form domains on the appropriate lengthscale when blended with an acceptor.[21] As a simple homopolymer, only one monomer is needed, the synthesis is facile and comparatively cheap to most alternative donor polymers, and P3HT has been synthesized in flow with excellent control over the molecular weight (M_w), polydispersity index (PDI) and regioregularity (RR).[22] Whilst the best performing single-junction P3HT devices are not able to replicate the >10% PCEs seen with a number of the push-pull copolymers, they have been reported to achieve respectable efficiencies of 5-7% to date.[23,24] With further focus on designing new acceptors to pair with P3HT, and careful optimization of such systems, it is likely that P3HT-based OSCs can present a strong case for commercialization, by improving upon the PCE and stability that can be achieved.
In this report we document the progress made in P3HT-based solar cells and discuss the impact that the molecular weight of P3HT has upon device performance when paired with two NFAs; O-IDTBR and EH-IDTBR.

2. P3HT:Fullerene Organic Solar Cells

As discussed above, fullerene derivatives were considered the prime candidates to use as electron acceptors in OSCs for several years, due to their favorable charge transport and electron accepting properties. PC$_{61}$BM was among the first reported fullerene derivatives with acceptable solubility by the inclusion of an ester-based side chain. The relatively good charge transport properties, photon harvesting and ready availability of P3HT, coupled with the excellent electron accepting properties and processability of PC$_{61}$BM have led to P3HT:PC$_{61}$BM becoming the most thoroughly studied system in OSCs, with over 1000 publications discussing this blend by 2010.[25] The structures and energy levels of the fullerene acceptors discussed herein are summarized in Figure 1.

Early attempts at P3HT:PC$_{61}$BM bulk heterojunction solar cells were able to achieve a PCE of 2.8%, though the formation of a suboptimal morphology was thought to be limiting the device performance.[26] This was subsequently improved by the use of thermal annealing, allowing rearrangement in the blend to form a nanoscale network of pure domains and improved crystallinity of the polymer.[27] This led to a substantial improvement in the FF and J$_{SC}$ by improving the charge carrier mobilities and reducing non-geminate recombination in the blend, resulting in substantial improvements in both the J$_{SC}$ and FF (8.5 mA cm$^{-2}$ and 0.60), and thus the achievement of PCEs up to 3.5%. A further development was the reduction in the P3HT:PC$_{61}$BM ratio to avoid the formation of micrometer sized PC$_{61}$BM aggregates during annealing, this allowed longer annealing of the thin films and at temperatures up to 150 °C, resulting in further improvement in devices, achieving a PCE of 5.0%.[28]
One major drawback of P3HT:PC₆₁BM cells is their large voltage losses, defined as
the difference between optical bandgap divided by elementary charge and the actual open-
circuit voltage, i.e. \( V_{\text{loss}} = \frac{E_{\text{gap}}}{q} - V_{\text{OC}} \), which has the value of 1.35V for P3HT:PC₆₁BM
devices. Analysis of voltage losses using the principle of detailed balance between light
absorption and emission allows the ideal open-circuit voltage to be calculated for any
absorber material, both in the case of a sharp absorption onset (i.e. the \( V_{\text{OC}} \) in the Shockley-
Queisser (SQ) limit \( V_{\text{OC,SQ}} \))\(^{[29]}\) and in the case of the non-sharp, actual absorption profile
\( V_{\text{OC,rad}} \).\(^{[30]}\) The deviation of \( V_{\text{OC}} \) from the SQ limit is then quantified by two loss terms, a
loss which is effectively due to the energetic offset between the absorption onset energy
and the charge transfer state energy of the organic heterojunction \( (\Delta V_{\text{OC,abs}} = V_{\text{OC,sq}} - V_{\text{OC,rad}}) \),
and a loss due to non-radiative recombination \( (\Delta V_{\text{OC,nrad}} = V_{\text{OC,rad}} - V_{\text{OC}}) \). Whilst the non-
radiative \( V_{\text{OC}} \) loss is similar among good-performing organic solar cells at around 0.4 V (0.38
V for P3HT:PC₆₁BM), the first of these losses varies strongly among material combinations
and is particularly high for P3HT:PC₆₁BM devices where it reaches 0.67V. This large
\( \Delta V_{\text{OC,abs}} \) loss for P3HT:PC₆₁BM could be reduced by replacing the fullerene with another
acceptor with a better LUMO-LUMO alignment with the P3HT, potentially increasing the
open circuit voltage by a significant amount. \( \Delta V_{\text{OC,nrad}} \) is related to the external LED
quantum efficiency of the devices \( (\Delta V_{\text{OC,nrad}} = -kT/q \ln(\text{EQE}_{\text{EL}}) \) that is the ratio between the
radiative and total recombination current (radiative + non-radiative). Therefore an increase in
\( \Delta V_{\text{OC,nrad}} \) can be interpreted as an increase of the non-radiative recombination current as
compared to the radiative one.

Efforts on addressing these problems have led to the development of a number of other
fullerene adducts with improved absorption in the visible region of the solar spectrum and
higher lying LUMOs. Phenyl-C₇₁ butyric acid methyl ester is analogous to PC₆₁BM but
instead makes use of the lower symmetry C₇₀ fullerene. The cause of PC₆₁BM’s poor optical
properties is the inclusion of the highly symmetric C₆₀ fullerene, which results in a number of
\(\pi-\pi^*\) transitions being disallowed. By replacing this symmetric C\(_{60}\) with the less symmetric C\(_{70}\) fullerene, there are fewer disallowed optical transitions, and thus higher extinction coefficient and lower wavelength absorption. The result of the improved photon harvesting has been shown to improve the photocurrent achieved in P3HT:PC\(_{71}\)BM devices, relative to reference devices containing PC\(_{61}\)BM.\(^{[31]}\) Indene-C\(_{60}\) bisadduct (IC\(_{60}\)BA) is another modified fullerene, with two electron-donating indene units adducted to its surface, the effect of this is to raise its LUMO by 0.17 eV, relative to PC\(_{61}\)BM.\(^{[32]}\) In initial devices, IC\(_{60}\)BA was able to achieve a PCE of 5.44\%, exceeding the best performing P3HT:PC\(_{61}\)BM devices. This is in a large part due to the vast increase in \(V_{OC}\) (0.86 V), afforded by the higher-lying LUMO of IC\(_{60}\)BA. Further optimization of the donor:acceptor ratio and annealing conditions led to an improved FF (increasing from 0.67 to 0.72), a result of an improved blend morphology, and allowing devices to reach PCEs as high as 6.6\%.\(^{[33]}\) Similar to PC\(_{61}\)BM, the inclusion of the highly symmetric C\(_{60}\) cage in IC\(_{60}\)BA limited the optical absorption possible when using this acceptor and therefore the C\(_{70}\) analogue, indene-C\(_{70}\) bisadduct (IC\(_{70}\)BA) was developed. Like IC\(_{60}\)BA, this acceptor also has a raised LUMO relative to PC\(_{61}\)BM, but also displays improved photon absorption. P3HT:IC\(_{70}\)BA devices were able to demonstrate enhanced performance, with a PCE of 6.7\%, due to improved photocurrent in devices.\(^{[34]}\) The use of a high-boiling solvent additive, 1,8-diiodooctane (DIO), allowed the blend to adopt an interpenetrating network of donor and acceptor domains and enhanced absorption in the blend, as such, devices were able to reach 7.4\% PCE.\(^{[7]}\)

The fabrication of ternary solar cells is another approach that has been used in an attempt to improve the performance of P3HT:fullerene devices. The addition of a third component to the active layer blend can be used to improve the spectral coverage achieved by a blend, or to increase the \(V_{OC}\) that can be achieved. A second fullerene based electron acceptor has been added to P3HT:PC\(_{61}\)BM binaries in a number of successful ternary OSCs. The use of fullerenes possessing higher lying LUMOs than PC\(_{61}\)BM is common in order to
boost the \( V_{OC} \) in the ternary system, however the use of self-organizing fullerenes such as PCBPy, F-PCBM and PCBDAN were successfully used to improve the blend morphology.\(^{35-37}\) In each case, improvements in \( J_{SC} \), \( V_{OC} \) and FF were reported, relative to the P3HT:PC\(_{61}\)BM reference binary devices, and thus each ternary was able to improve on the PCE by at least 25\%. PCBPy, F-PCBM and PCBDAN each utilized a different approach in order to control the blend morphology; PCBPy self-aggregated to form interpenetrating nanostructures in the blend, F-PCBM altered the vertical phase separation to form a buffer layer at the top of the thin film, and the high surface energy PCBDAN formed a cathode interface in inverted devices. All of these examples displayed the potential influence that a third component can have on improving the morphology in order to benefit the device performance. However, the low efficiencies exhibited in each case (< 5\%) limited their interest and applicability, especially when the added complexity of optimizing a ternary system is taken into consideration. Nonetheless, these fullerene ternaries paved the way for future studies into three component bulk heterojunctions, yielding greater success.

Whilst the above approaches have successfully improved the PCE that P3HT:fullerene solar cells are able to achieve they have not addressed the morphological instability exhibited by fullerene-containing solar cells. Moreover, whilst the use of fullerene multiadducts has helped to raise the device open-circuit voltage relative to P3HT:PC\(_{61}\)BM devices, the \( V_{OC} \) losses are still significant. Regarding the morphological instability, fullerene derivatives have been shown to diffuse through the active layer over time; forming large micrometer aggregates that lead to increased exciton relaxation losses, and in some cases fullerene migration to the device electrodes, resulting in delamination of the thin film and device failure.\(^{10,38}\) Without preventing this morphological instability, fullerene-containing OSCs would be potentially unfeasible to produce commercially. The most commonly adopted strategy to overcome fullerene aggregation and migration over time is the use of cross-linking in the thin film. Chemical modification to either the P3HT or the fullerene can be carried out
to include cross-linkable functionalities such as azides, oxetanes and vinyl groups. Although this tactic has been shown to successfully reduce the migration of fullerenes in blends by up to an order of magnitude, it is often accompanied by a drastic reduction in initial PCE and requires the synthesis or more expensive analogues of P3HT or fullerenes.[39] Photodimerization of fullerenes is another tactic that can be used to improve the morphological stability of fullerene-containing OSCs, as upon dimerization the aggregation tendency is noticeably suppressed.[40]

In summary, although PC₆₁BM is among the most well understood electron acceptors to be paired with P3HT, its inherent issues have limited its performance to 5%, and with poor instability it remains unlikely to be a viable commercial option. Improved fullerene adducts have successfully improved upon the performance of PC₆₁BM, most notably IC₇₀BA, however the high synthetic costs to produce such acceptors, and remaining issues of morphological instability are concerning. The development of ternary OSCs, in which another acceptor component is added, in order to beneficially alter the blend morphology, have been shown to successfully enhance device performance in relation to the binary devices and are significant in the development of > 7% PCE P3HT OSCs. Despite this, fullerenes are unable to produce high performing stable devices, with P3HT, and a need for new electron accepting materials has become apparent in recent times.

3. P3HT:NFA Organic Solar Cells

In an attempt to replicate the excellent electron transport properties exhibited by fullerenes while simultaneously producing highly absorbing materials, many of the first NFAs were planar small molecules with extended π-conjugation, such as perylene diimides and truxenones. A result of the use of extended fused ring systems present in these small molecules was that they were highly crystalline. Whilst this strategy was successful in achieving materials capable of good electron transport and strong light absorption in the
visible region, many of these acceptors worked poorly in bulk heterojunction devices due to the formation of excessively large aggregates and domains in the blend.\cite{14,15} When paired with crystalline P3HT this issue was compounded further, as the two components would have little tendency to mix, forming microscale P3HT and acceptor domains, which are unsuitable for efficient exciton separation and charge generation in the blends, leaving P3HT an inappropriate candidate to use with such acceptors.\cite{41} There are few examples of working OSCs when perylene diimide based acceptors have been blended with P3HT, the best being 1.7% PCE devices using a benzodithiophene bridged perylene diimide dimer Bis-PDI-BDT-EG.\cite{42} A highly twisted conformation along the backbone allowed aggregation nanoscale aggregation, with domains of 10-20 nm present in the blend. Another rotationally symmetric acceptor, diindenorubicene (DIR-2EH), was able to achieve PCEs of up to 3% with P3HT. This was aided by the inclusion of four bulky 2-ethylhexyl solubilizing chains close to the planar core to suppress excessive π-π stacking.\cite{43} However, in order to produce OSCs capable of achieving competitive PCEs, careful consideration is needed to select an appropriate donor polymer to blend with these crystalline acceptors. Perylene diimide NFAs have been most successful when blended with less ordered polymers such as PTB7-Th and PDBT-T1.\cite{16,44}

As anticipated from the tuneability of their LUMO energy, NFAs have allowed a strong reduction of the VOC losses in organic solar cells.\cite{45} Using FBR and IDTBR Baran et al. showed a significant decrease in the voltage losses of PffBT4T-2DT based solar cells.\cite{46}

Upon changing the acceptor from PC71BM to fluorene, indenofluorene and indacenodithiophene based NFAs (FBR, IDFBR and IDTBR respectively), VOC,rad increased by 0.2 V and ΔVOC,nrad decreased by 0.06V. The improvement in VOC was accompanied by an improvement of the overall PCE of the cell from 7.5% to 9.9%. The low voltage losses achieved with NFAs will further improve the performance of BHJ solar cells beyond the polymer: fullerene.
A-D-A type nonfullerene acceptors have had a great deal more success when paired with P3HT. These acceptors have much lesser aggregation tendencies than the perylene diimides, and are therefore able to mix sufficiently with P3HT to form nanoscale morphologies in a number of cases. The first A-D-A type acceptor that was capable of achieving a PCE of 3% when paired with P3HT was Flu-RH. This acceptor consisted of a fluorene core flanked on either side by thiophene units on either side and capped with the well-known dye moiety 3-ethylrhodanine on the periphery, affording a medium bandgap (2.1 eV) acceptor.[47] The inability to exceed the efficiency of P3HT:PC61BM can be attributed to a couple of notable factors: (i) P3HT and Flu-RH absorb in the same region of the solar spectrum, mitigating the added photon harvesting capabilities that the acceptor possesses over fullerenes, and thereby limiting the photocurrent that was achieved (5.7 mA cm⁻²) and (ii) the poorer electron transport properties of Flu-RH, in comparison to PC61BM, and sub-optimal blend morphology which is at least partly responsible for the low FF achieved (0.52). However, the acceptor possesses a far higher lying LUMO than the fullerene derivatives (-3.5 eV) which resulted in a substantially higher Voc of 1.03 V to be achieved, illustrating the potential of NFAs to surpass fullerenes. A similar acceptor, FBR, was able to improve upon the promising performance of Flu-RH, achieving a PCE of 4.1% when blended with P3HT.[48] FBR consists of a fluorene core flanked by benzothiadiazole (BT) and rhodanine units; the inclusion of an electron deficient π-conjugated spacer acted to increase the push-pull character in this acceptor, leading to stronger photon absorption in the blend. The BT spacer also causes FBR to adopt a twisted structure, the steric clash of ortho-hydrogens in a phenyl-phenyl link are much greater than those of a phenyl-thienyl link, and thus FBR twists to avoid these steric clashes. Despite possessing a deeper LUMO (-3.6 eV) and therefore a lower Voc of 0.82 V, FBR was able to achieve a greater PCE by achieving a significantly improved JSC (8.0 mA cm⁻²). FBR is also a medium bandgap acceptor that absorbs in the same region of the solar spectrum as P3HT. However, respectable charge carrier mobilities in the blend were reported,
which are likely to have contributed to the improved photocurrent and FF observed in these cells. The twisted backbone of FBR rendered it a relatively amorphous material, as such it became thoroughly mixed in the P3HT and was unable to form nanoscale domains, leading to large geminate recombinative losses. The amorphous nature of FBR was beneficial, however, when comparing the thermal stability of P3HT:FBR films to P3HT:PC\textsubscript{61}BM. The greatly reduced tendency for FBR to self-aggregate resulted in the blend morphology being maintained after 12 hours of annealing at 140 °C, whereas the P3HT:PC\textsubscript{61}BM blend formed microscale aggregates after just 1 hour of annealing.

To induce crystallinity, and therefore avoid molecular mixing of the NFA within the P3HT, A-D-A acceptors with increased planarity were developed. Additionally, moieties that invoked stronger push-pull hybridization were required in order to narrow the bandgap of the acceptor such that it was able to provide complementary absorption to P3HT. IDTBR is analogous to FBR, however the fluorene core was replaced with the more electron-rich indacenodithiophene (IDT) unit.\textsuperscript{[23]} The IDT core forms thienyl-phenyl links with the neighboring BT units, and the lack of steric clashes between ortho-hydrogens allows IDTBR to adopt a planar conformation. The greater electron donating character of the IDT core, coupled with increased planarity, and therefore greater conjugation in the acceptor, lead to a large reduction in the bandgap of IDTBR to 1.6 eV. When blended with P3HT, IDTBR was able to achieve a substantially improved PCE of 6.4%, which can be attributed to improved photon harvesting across the solar spectrum, since IDTBR absorbs strongly in the 650-750 nm region, leading to a vast improvement in the photocurrent (14.1 mA cm\textsuperscript{-2}). Also, the greater planarity of IDTBR afforded it a greater tendency to aggregate, which thereby led to the formation of IDTBR and P3HT domains in the active layer blend, substantially reducing the non-geminate recombination in this blend. Two analogues of IDTBR were reported, one with four n-octyl solubilizing chains on the IDT core (O-IDTBR) and another with four branched 2-ethylhexyl solubilizing chains (EH-IDTBR). Though both were able to achieve PCEs of
over 6%, the O-IDTBR gave a slightly better performance; with suggestions that its greater tendency to aggregate cause a broadening of its absorption, and therefore external quantum efficiency (EQE), leading to a greater J_{SC} in devices.\cite{23} Another low-bandgap A-D-A acceptor, H1, consists of a bifluorenylidene core linked to four, thiophene flanked, diketopyrrolopyrrole units to form an H-shaped acceptor.\cite{49} P3HT:H1 devices were able to produce a photocurrent of 7.7 mA cm\textsuperscript{-2} and a FF of 0.60, however the standout feature of these devices was an exceptional V_{OC} of 1.17 V. This demonstrates that acceptors with appropriately positioned energy levels can maximize the V_{OC} and despite poor photocurrent, as a result of the donor and acceptor displaying complementary absorption to one another, devices were still able to achieve very competitive PCEs of 5.4%. Similarly, BTA1 is another acceptor that was able to achieve an impressive V_{OC} in devices. This acceptor further built upon the design principles of the IDTBR acceptors; making use of the benzotriazole moiety, rather than benzothiadiazole, in order to raise the LUMO of the acceptor.\cite{50} BTA1 still maintained a planar backbone, and therefore still possessed competitive electron mobilities when blended with P3HT. A result of the high lying LUMO was the achievement of a V_{OC} of 1.02 V, whilst still achieving a photocurrent of 7.3 mA cm\textsuperscript{-2} and a FF of 0.70, which overall lead to PCEs of 5.2%. A similar absorption spectrum to P3HT, and suboptimal morphology in the bulk heterojunction were the likely reason for the low J_{SC} leaving room for future improvement in the design of these NFAs. It must be noted that one of the best performing NFAs, ITIC, does not work well in P3HT OSCs; only able to achieve a PCE of 1.2%.\cite{51} The disappointing performance can be linked to an unfavorable blend morphology, since both the energy level alignment and optical absorption properties meet the requirements for producing efficient OSCs. ITIC disrupts the packing of P3HT so severely that the blend maintains an amorphous morphology with no distinct domains even after annealing. The development of a more strongly aggregating analogue of ITIC might allow the formation of the necessary nanoscale morphology, which would lead to an improved performance in OSCs.
The ternary approach has also been used successfully in P3HT:NFA devices to improve upon the impressive performance displayed by the P3HT:IDTBR binary OSCs. A second NFA, IDFBR, was added to the blend in a ratio of 1:0.7:0.3 (P3HT:IDTBR:IDFBR), with the aim of improving spectral coverage for photon harvesting and increasing the maximum $V_{oc}$ that devices could achieve.\cite{24} Consisting of an indenofluorene core, flanked by BT and 3-ethylrhodanine units, IDFBR possesses a medium bandgap, thereby providing complementary absorption to IDTBR, and a higher lying LUMO (-3.7 eV vs –3.9 eV). Another interesting feature of IDFBR is a twisted backbone, similar to FBR, resulting in a less strongly aggregating acceptor. The consequence of which was the formation of P3HT and IDTBR domains in the blend, where IDFBR was only present in mixed regions with either the polymer or second acceptor. It is suggested that this three-phase microstructure is favorable for photocurrent generation and yields a higher-lying electron transport level, which yields a greater $V_{oc}$ in devices. The IDFBR, which exists mainly in mixed regions between the P3HT and IDTBR crystalline domains, helped to form an energetic impediment to recombination, leading to a reduction in the observed recombination losses in the system. Overall, this resulted in a simultaneous improvement in $J_{sc}$, $V_{oc}$ and FF relative to the P3HT:IDTBR binary, yielding a maximum PCE of 7.8\%, the highest reported for single junction OSCs with P3HT. The P3HT:IDTBR:IDFBR ternary OSCs exhibited remarkably higher shelf life and photostability in comparison to a number of polymer:PC$_{60}$BM, including polymers such as PTB7-Th and PffBT4T-2OD. The synergistic effect of improving the J-V characteristics and stability of OSCs with the inclusion of an additional acceptor leaves this approach a promising one in the development of highly stable and scalable OSCs with competitive PCEs.

In short, the development of NFAs has led to significant improvement in P3HT-based OSC performance, as well as reduced voltage losses. Several NFAs have managed to exceed the PCE exhibited by PC$_{61}$BM, and a few NFA devices have managed to surpass the record PCE in P3HT devices formerly held by P3HT:IC$_{70}$BA. The structures and energy levels of the
NFAs discussed above have been summarized in **Figure 2**. In tandem with the ability to match or surpass the performance of fullerene-containing OSCs, many of the NFA devices have exhibited far greater morphological and photostability, leaving them more promising candidates to be used in commercial applications. The report of a fullerene-free ternary system with an impressive PCE and stability highlights the promise of such systems. However, recent trends in designing NFAs that work well with a number of the medium and low bandgap high performance polymers have led to a lull in the development of acceptors designed to work well with P3HT. This is an area which could prove vital to producing OSCs which are capable of being upscaled, and so more effort should be directed to producing NFAs that can further improve upon the reported P3HT:NFA devices.

**4. Molecular Weight Dependence in P3HT Organic Solar Cells**

In most cases, the primary considerations to select an appropriate donor polymer to pair with an electron acceptor have been optoelectronic in nature. Though such considerations are of great significance, the microstructural characteristics of the polymer:small molecule blends should also be assessed to ensure optimal device performance can be attained. The influence of the molecular weight (Mₘ) of the polymer, on device performance, has been probed in fullerene-containing devices, but very few studies involving fullerene-free OSCs have been undertaken.

When investigating the effect of molecular weight on the J-V characteristics in P3HT:PC₆₁BM devices, it has been suggested that an optimal Mₘ within the range of 15-40 kDa provided the best device performance.[52] It was noted that lower or higher P3HT Mₘ was detrimental to solar cell performances in P3HT: PC₆₁BM devices. Another study obtained a variety of molecular weight batches of P3HT with virtually identical RR, and came to a similar conclusion, that a molecular weight of between 20-30 kDa was optimal for use in bulk heterojunction P3HT:PC₆₁BM cells.[53]
Molecular weight impacts the charge mobility of P3HT. Increasing molecular weight has been reported to increase mobilities in the range of 2 to 19 kDa\textsuperscript{[53]} to 3 to 40 kDa\textsuperscript{[54,55]} as measured in field-effect transistors while decreasing mobilities in the range of 13 to 121 kDa as measured by time-of-flight techniques. This points towards an optimum in the middle range P3HT M\textsubscript{w}, although it must be noted that the mobilities of the lowest studied M\textsubscript{w} are sensitive to processing. When the processing was optimized, the films for the lower P3HT M\textsubscript{w} were observed to form highly ordered nanorod structures, whereas the middle range M\textsubscript{w} P3HT formed less ordered isotropic nodule structures\textsuperscript{[54,55]}. No direct correlation between crystallinity and mobility was found but it was rather suggested that the mobility of the low M\textsubscript{w} P3HT was limited by a combination of disorder at the grain boundaries and the inherent effects of chain lengths. Low M\textsubscript{w} P3HT also contains a higher density of chain-ends and defects arising during their synthesis, both of which have been shown to act as traps and may also account for the observed reduced mobilities. For higher M\textsubscript{w}, chains start participating in different aggregates leading to an increase in interconnection between high mobilities aggregates. For very high M\textsubscript{w}, since the polymer chains are much longer, they possess much higher viscosity, and are more likely to entangle with one another, hindering crystallization.

Whilst M\textsubscript{w} affects the hole mobility in P3HT, variations in efficiency of P3HT:PC\textsubscript{61}BM solar cells could not be assigned solely to changes in hole mobility, and it was suggested that active layer morphology was also likely to play a role\textsuperscript{[52]}. As an example of the effect of M\textsubscript{w} dependent microstructure on device performance, the greater crystallinity of low M\textsubscript{w} P3HT has been shown to lead to a decrease in charge transfer state energy, and therefore a corresponding decrease in the open circuit voltage\textsuperscript{[56]}. Another consequence of the greater degree of crystallinity in the low M\textsubscript{w} P3HT was stronger light absorption, especially at longer wavelengths, which resulted in greater short circuit current in devices\textsuperscript{[56]}. Polymer M\textsubscript{w} dependent effects on solar cell PCE have been observed in other systems. One study focused on the dependence of PBDTT-FTTE:perylene diimide device performance on polymer M\textsubscript{w}.
and the crystallinity of the perylene diimide acceptor.\textsuperscript{[57]} It was found that the most crystalline acceptor suppressed the PCE $M_w$ dependence by dominating the morphology formation during processing, while blends incorporating the less crystalline acceptors led to different trends in PCE with varying $M_w$.

The influence of the RR of P3HT has also been explored in fullerene-containing OSCs; highly regioregular P3HT batches ($>98\%$) possess a greater degree of crystallinity in neat films, though it is uncertain whether this improves the ordering, and therefore charge carrier mobilities in blends.\textsuperscript{[58,59]} Despite achieving lower PCEs initially, the use of less regioregular P3HT (86\%) has been reported to improve the thermal stability of P3HT:PC$_{61}$BM devices by hindering the crystallization-induced phase segregation of PC$_{61}$BM.\textsuperscript{[60]}

It was therefore important to explore whether these relationships were also prevalent in polymer:NFA blends. In this work, we compared five batches of P3HT, with a variety of molecular weights, to elucidate any relationship between $M_w$ and device performance when used in bulk heterojunction OSCs with two NFAs; namely O-IDTBR and EH-IDTBR. The five P3HT batches, detailed in Table 1, were selected to span a wide variety of $M_w$ values, whilst keeping the RR relatively constant. It must be noted that there are some variations in the polydispersity index (PDI) of the batches. However, we do not believe that this small PDI variation complicated our observations. The two different NFAs were selected because of differences in their crystallinity: previous reports have shown that O-IDTBR is more crystalline in nature than EH-IDTBR, its branched chain analogue.\textsuperscript{[23]}

An inverted architecture was utilized to fabricate all devices, as per previous reports using these NFAs.\textsuperscript{[23,24]} As can be seen from Figure 3b and Table 2 the performance of P3HT:O-IDTBR devices displays a strong dependence on the polymer $M_w$, with a maximum PCE of 7.0\% being achieved using P3HT-C (34 kDa), and lower PCE being observed in both higher and lower $M_w$ P3HT batches. Similar to the findings in P3HT:PC$_{61}$BM devices, the
lower M_w P3HT led to a reduced $V_{OC}$; with P3HT-A only able to achieve 0.67 V, over 50 mV lower than the $V_{OC}$ achieved with the higher M_w P3HT batches. Upon increasing the P3HT M_w from 34 kDa to 94 kDa the photocurrent decreases from 14.6 to 12.1 mA cm$^{-2}$ However, the lowest M_w P3HT, batches A and B, were only able to achieve a photocurrent of 11.8 and 12.0 mA cm$^{-2}$ respectively. This is considerably lower than those achieved with the higher M_w P3HT-C, which is contrary to the trend observed in fullerene-containing devices reported previously.$^{[56]}$ P3HT-A exhibited significantly lower FF values than the highest performing P3HT C devices (0.50 and 0.66 respectively). The higher M_w batches achieved slightly lower FF values of 0.62. Interestingly, when O-IDTBR is replaced with the less crystalline analogue, EH-IDTBR, as the electron acceptor, the strong dependence of device performance on the M_w of P3HT was not observed. As Figure 3c and Table 2 show, the J-V characteristics of devices using all five P3HT batches are virtually identical, with all devices able to achieve a PCE of approximately 6%. Figure S1 clearly shows that each of the P3HT batches were able to achieve very similar J_Sc and $V_{OC}$ in devices. The FF of P3HT:EH-IDTBR devices using P3HT A is marginally lower than those using the higher M_w polymers, however this is a substantially smaller difference than was observed in O-IDTBR devices. Although the P3HT:EH-IDTBR devices were not able to match the 7% attained by the P3HT-C:O-IDTBR blends, the insensitivity that EH-IDTBR exhibits to P3HT M_w may render it a more versatile NFA when used with P3HT. We hypothesize that these observations are linked with the dependence of blend microstructure on polymer M_w.

To better characterize the M_w dependence of the photovoltaic performance of our P3HT:O-IDTBR devices, we analyzed the contributions to the voltage loss relative to the voltage of ideal devices, using luminescence spectroscopy.$^{[30]}$ In this approach the principle of reciprocity between photon absorption and emission is used to quantify the radiative and non-radiative voltage losses via measurement of the EQE and electroluminescence (EL).$^{[30,61]}$ Photoluminescence (PL) spectra showed that the excitonic state energy lies at around 1.55 eV.
in every case (see Figure 4a). This value is consistent with the absorption onset energy as estimated from the EQE when plotted on a linear scale (not shown). Figure 4b shows the normalized EL spectra of the devices based on different P3HT M_w. We see a clear broadening effect of the spectrum as M_w increases from 17 to 34 kDa before narrowing again for the higher M_w batches of P3HT. This is also reflected in the EQE measurements (see Figure 5a), where the EQE edge broadens as M_w increases, peaking in the 34 kDa P3HT device and subsequently narrowing in the 64 and 94 kDa P3HT devices. The observed broadening in the EL and EQE for the 34 kDa P3HT device leads to a lower radiative limit to V_{OC}, V_{OC,rad} and since the optical gap and the corresponding Shockley-Queisser limit to V_{OC} (V_{OC,SQ}), does not change, it leads to a greater voltage loss due to broadening of the absorption edge ΔV_{OC,abs}. These contributions to the voltage loss are shown in Figure 3b. However, the effect of M_w on ΔV_{OC,abs} is relatively small compared to the effect on the non-radiative voltage loss, ΔV_{OC,nrad} (defined as V_{OC,rad}-V_{OC}). The resulting voltage losses are summarized in Table 3, where the 34 kDa P3HT device shows the highest ΔV_{OC,abs} (0.15 V), but the lowest ΔV_{OC,nrad} (0.39 V). Since the absorption broadening voltage loss in this system is relatively small (less than 0.15 V compared to 0.3-0.5 eV for the non-radiative loss), we can conclude that non-radiative recombination limits the V_{OC} of the cells. Accordingly, the best device also shows the lowest non-radiative voltage loss. The improvement in the non-radiative voltage losses are due to an enhanced LED quantum efficiency of the cell, where the ratio between radiative and non-radiative recombination rate increase. The best P3HT:O-IDTBR shows a ΔV_{OC,nrad} similar to that of P3HT:PC_{61}BM, but much lower overall voltage loss, i.e. 0.81 V versus 1.35 V. The significant improvement in the V_{OC} losses is mainly due to the reduced broadening of the EQE edge, compared to that of P3HT:PC_{61}BM.

Time delayed collection field (TDCF) measurements were conducted on three of the P3HT:O-IDTBR blends (P3HT-A, P3HT-C and P3HT-E) to investigate the field dependence
of charge generation.\textsuperscript{[62]} The acquired data for the total charge ($Q_{\text{tot}}$) of the three selected blends is presented in Figure 6 and plotted alongside the J-V curves of the respective pixels of the devices used for TDCF measurements. Clearly, the total photo-generated charge $Q_{\text{tot}}$ decreases with increasing (from -2 to $V_{\text{oc}}$) pre-bias, indicating weakly field-dependent charge carrier generation. However, it appears that in the P3HT-A (17 kDa) device, charge generation is more strongly field dependent than in the other two systems. This suggests that charge generation is most marginal, and therefore benefits most from applied electric field, in the low M$_w$ case. In all three cases the field dependence of charge generation resembles the slope of the J-V curves of the respective devices, suggesting that the fill factor of all three systems may be influenced by the field dependence of charge generation. Note that this method only probes the field dependence of charge pair generation and prompt (geminate) recombination; beyond the maximum power point, non-geminate recombination losses dominate as extraction becomes slower and for this reason the J-V curves deviate from the bias dependence of $Q_{\text{tot}}$ obtained from the TDCF experiment. Polymer:fullerene blends have been previously studied by this technique.\textsuperscript{[63]} It was observed that systems with larger and purer domains lead to more efficient and less field-dependent photogeneration. Moreover, individual, large domains might be (slightly) bias dependent in blends processed without any additives.\textsuperscript{[64]} However, for the case of NFA, no studies relating the domain size with field dependent charge generation have been reported.

In an effort to understand the PCE dependence on M$_w$ for the O-IDTBR systems, and M$_w$ independence in the P3HT:EH-IDTBR devices, the phase behavior of the binary blends of these materials was investigated using differential scanning calorimetry (DSC) to construct the non-equilibrium phase diagram for each binary. The endset of the melting transition at each composition was used to construct the liquidus. Note that to obtain the phase diagrams, the samples are drop-cast. The phase diagrams deduced from the DSC measurements for four P3HT batches (P3HT-B, P3HT-C, P3HT-D and P3HT-E) blended with O-IDTBR, and the
three batches of P3HT with EH-IDTBR (P3HT-B, P3HT-C and P3HT E) are depicted in Figure 7. Eutectic behavior was observed for both blend systems at all studied molecular weights. Figure 5 shows that in the case of P3HT:O-IDTBR, the eutectic composition becomes increasingly rich in O-IDTBR as the molecular weight of P3HT increases (40 to 60 wt% O-IDTBR on increase of M\textsubscript{w} from 20 to 94 kDa) while for EH-IDTBR, the eutectic composition is insensitive to molecular weight. The active layer composition (1:1 P3HT:O-IDTBR) is hyper-eutectic when expressed in terms of the fraction of O-IDTBR for low molecular weights including the best performing device (with 34 kDa) while it is hypo-eutectic for higher M\textsubscript{w}. In the case of EH-IDTBR, the active layer composition is hyper-eutectic regardless of M\textsubscript{w}. In P3HT:PC\textsubscript{61}BM blends, the optimal P3HT:PC\textsubscript{61}BM ratio was found to be slightly hyper-eutectic.\cite{65} It was suggested that the excess acceptor is required to ensure the formation of percolation pathways which improve electron collection at the cathode.\cite{65,66} The eutectic composition of P3HT:PC\textsubscript{61}BM also becomes increasingly rich in PC\textsubscript{61}BM with increasing P3HT M\textsubscript{w} but for all P3HT M\textsubscript{w}, 1:1 is always hyper-eutectic.

Furthermore, the absence of a clear melting transition around the eutectic composition for P3HT:EH-IDTBR (see Figures S6-S8) indicates either that the mixture is mainly amorphous or that the crystals are too small (nanometer size) to be detected by DSC. This can also be seen in the phase diagram where a significant jump in the melting point depression is observed between 20 and 50 wt% EH-IDTBR for the blend with 20 kDa P3HT, and between 20 and 30 wt% in the highest M\textsubscript{w} blend. This suggests that the P3HT:EH-IDTBR blends are significantly more amorphous in these composition windows, which might explain insensitivity of the eutectic composition to polymer M\textsubscript{w}. In contrast, the jump in melting point depression in blends with O-IDTBR occurs within the range of 20 to 40 wt% O-IDTBR for the 20 kDa P3HT but is absent in the higher M\textsubscript{w} blends, which also show a maximum melting point depression at higher O-IDTBR contents. This difference in behavior between the blend systems aligns with the fact that O-IDTBR is a more crystalline acceptor than EH-IDTBR,
leading to a stronger competition between polymer and acceptor crystallization in the blends, hence a variation in eutectic composition with polymer $M_w$.

In order to further relate P3HT:O-IDTBR phase behavior with device performances, we use a series of imaging techniques to study different lengthscales relevant to various device properties. Atomic force microscopy (AFM) was used to investigate the surface features of the P3HT: O-IDTBR blends. The presence of micron-size features in the blends films was observed, as shown in Figure 8a. The size of the features decreases slightly with increasing P3HT $M_w$. Each of the samples exhibited a similar surface roughness, in the range of 17-21 nm. To complement AFM, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used to probe the blend morphology, on the lengthscale of the features observed by AFM, in P3HT:O-IDTBR. Figure S9 shows HAADF-STEM images of four samples that were acquired in the in-plane-view direction. The analysis revealed the presence of domains of several tens of nanometers (nm) in size. Interestingly, the P3HT-C (34 kDa) and P3HT-D (64 kDa) blends showed relatively small and discrete domain sizes, uniformly distributed throughout the film. By contrast, P3HT-E (94 kDa) showed relatively large domains, in the range 80 nm or more. Meanwhile, in case of P3HT-A (17 kDa), a broad distribution of different size domains was observed without clarity. Core-loss electron energy-loss spectroscopy (EELS) was used to gain further insight into the apparent blend composition in these domains (see the RGB composite of sulfur (S) and nitrogen (N) maps shown in Figure 8b). Firstly, these domains are not pure domains. Some phase separation occurs on the lengthscale of tens of nanometres between P3HT-rich domains and O-IDTBR-rich domains. Increasing the $M_w$ from 34 kDa to 94 kDa lead to larger domains with richer O-IDTBR phase. It is pertinent to note that these observations were made in the in-plane-view direction, and hence they provide no information in regard to changes in the composition with depth. In order to gain further insight into the bulk morphology of these blends, HAADF-STEM analysis of cross-section specimens was also performed, shown in
Figures S9 and S10. Note that the size of the provided cross-sectional micrograph (60x60 nm) is smaller than the in-plane micrographs (600x600 nm) and are therefore at the lengthscale of the phase separation. At this scale, no further phase separation is observed in the vertical direction and the micrographs are homogeneous. EELS shows that the domains are not pure, and contain increasingly O-IDTBR rich phases when increasing P3HT M<sub>w</sub> between 34 and 94 kDa. HAADF-STEM imaging of the cross-section specimens additionally determined the absolute thickness of the active layer, which for each analyzed sample, was in the range of 80-100 nm, with an average roughness of +/- 10 nm.

Grazing incidence wide-angle x-ray diffraction (GIWAXS) measurements were performed on a number of the neat P3HT batches (17 kDa, 34 kDa, 64 kDa and 94 kDa) and their blends with both O-IDTBR and EH-IDTBR respectively. The 2D GIWAXS line cuts of the in-plane (Q<sub>xy</sub>) and out-of-plane (Q<sub>z</sub>) directions are shown in Figure S12 and S13. In P3HT:O-IDTBR blends, the P3HT loses some edge-on texture but the packing habit of P3HT crystallites is the same as the neat P3HT film. The O-IDTBR domains are isotropically distributed, exhibiting polycrystalline rings in the 2D patterns. In P3HT:EH-IDTBR blends, the packing habit of the P3HT crystallites is also maintained, consistent with previous GIWAXS observations,[23] two new peaks at Q = 0.49 and 1.8 Å<sup>-1</sup> were present suggesting that EH-IDTBR crystallizes into a different polymorph or orients in a different direction upon blending. Overall, in O-IDTBR and EH-IDTBR blends there are no appreciable differences in the way P3HT stacks or its orientation with varying molecular weight.

In summary, the microstructure of P3HT:O-IDTBR blends is complex and presents features on different length scales. In particular, the microstructures observed for high M<sub>w</sub> polymers are likely more dominated by kinetics of drying rather than by thermodynamics. Although miscibility changes with molecular weight, the temperature dependence of the miscibility and the spinodal demixing behavior also change significantly. Therefore, drying rates and donor/acceptor mixing ratios become more relevant for the higher molecular weight
fractions. We observe micron-size features by AFM and phase-separation at the nanoscale between P3HT-rich and O-IDTBR-rich domains. While the size of the micron-size features decrease slightly with P3HT $M_w$, the phase separation at the nanoscale level seems to increase leading to more prominent O-IDTBR-rich domains with higher $M_w$. We suggest that at the lower P3HT molecular weights, the 1:1 ratio is hyper-eutectic leading to the formation of acceptor percolation pathways that lead to improve charge collection. Around these percolation pathways, the eutectic microstructure develop with nanoscale crystals of both P3HT and O-IDTBR, unlikely to be captured by DSC but measured by GIWAXS, and an amorphous mixture of P3HT and O-IDTBR. P3HT and O-IDTBR are likely to exhibit finite miscibility. Thus, we suggest that the phase separation observed at the nanoscale is due to a spinodal decomposition of the amorphous mixture of P3HT and O-IDTBR. The difference in nanoscale phase separation with P3HT $M_w$ is only a reflection of the change of eutectic composition. Thus, we suggest that P3HT-C combines the advantage of being hyper-eutectic, with associated good charge collection due to an acceptor percolation pathway, and an optimal phase separation at the nanoscale, leading to good charge generation. When the P3HT $M_w$ increases, the devices suffer from reduce charge collection due to a lack of acceptor percolation pathways; while when the P3HT $M_w$ is too low, the devices suffer from reduce charge generation due to a lack of phase separation at the nanoscale. This is summarized in Figure S14.

Interestingly, on the other hand, P3HT:EH-IDTBR blend devices do not exhibit the same sensitivity to P3HT molecular weight, but do not reach as high performance as the best optimized O-IDTBR devices.

5. Conclusions and Outlook

To conclude, considerable progress has been made in designing P3HT OSC systems. The established fullerene-containing devices have progressed from the use of simple soluble fullerenes, such as PC$_{61}$BM, to the use of less symmetric C$_{70}$ cages to improve light
absorption (PC\textsubscript{71}BM) and bis-adducts to raise the acceptor’s LUMO (IC\textsubscript{60}BA and IC\textsubscript{70}BA). These developments have led to the ability to achieve PCEs as high as 7.4% with IC\textsubscript{70}BA, though a high boiling additive was necessary to achieve the optimal morphology. Despite being unable to match the record performance in P3HT:fullerene OSCs, the use of ternary blends have also shown potential in device optimization, moving forwards. In several cases, the addition of a second acceptor into the blend has improved the blend morphology, leading to simultaneous improvements in J\textsubscript{sc}, V\textsubscript{oc} and FF. Issues of morphological instability still persist in fullerene devices owing to their strong aggregation tendency and leading to the formation of micrometer sized aggregates in blends over time. This has been successfully addressed with the use of cross-linking, however the improved stability is accompanied with a loss in PCE and the need for expensive cross-linkable acceptors. The stability issues, coupled with the large V\textsubscript{oc} losses exhibited in P3HT:fullerene OSCs, leave such blends unlikely to succeed.

The recent success of A-D-A nonfullerene acceptors have provided a promising alternative to fullerene acceptors. They have been designed to have higher lying LUMOs, improved photon absorption and a reduced aggregation tendency, thereby overcoming the issues that have limited fullerene acceptors. Though early A-D-A acceptors were unable to form domains on the correct lengthscale when blended with P3HT, due to their twisted structures, the development of planar acceptors such as O-IDTBR and H1 led to improved phase separation and complementary absorption, by narrowing the bandgap of the acceptors. P3HT:O-IDTBR devices were able to achieve a OCE as high as 6.4%, with impressive stability exhibited relative to fullerene-containing devices. This system was further developed with the addition of a third component, IDFBR, which led to the formation of a favorable three-phase microstructure, and OSCs that were able to achieve a maximum PCE of 7.6%. This progress has led to the record performance in single-junction P3HT devices, and paired with the excellent stability, renders P3HT:NFA blends likely to be among the most realistic
for commercialization, at present. However, many of the more recently reported NFAs have been designed to work well with low bandgap polymers. These polymers are not currently scalable on the industrial level and as such, more emphasis should be apportioned to developing new acceptors suited to perform well with P3HT.

This work on P3HT:IDTBR blends highlights the care that must be taken when optimizing P3HT:NFA OSCs. We observed a clear $M_w$ dependence on device performance in P3HT:O-IDTBR blends, and therefore suggest that it is pertinent to consider the ideal polymer $M_w$ to use in such systems. We propose that the optimal device performance (7.0%), when P3HT-C is used with O-IDTBR, is a result of improved acceptor percolation pathways and optimal phase separation at the nanoscale, in comparison to blends with either lower or higher $M_w$ polymer batches. This can be related to the competition between the crystallization of the P3HT and O-IDTBR, which varies with polymer $M_w$, as shown by the DSC measurements. When the less crystalline EH-IDTBR is used as the electron acceptor, no variation in device performance with $M_w$ was observed, though the maximum PCE was slightly lower (6.3%) than achieved with P3HT-C:O-IDTBR. A result of the reduced crystallinity of EH-IDTBR, in comparison to O-IDTBR, is the more amorphous nature of P3HT:EH-IDTBR blends. Hence, the competition between the crystallization of P3HT and EH-IDTBR is reduced significantly, leading to an apparent insensitivity to device performance. The fact that two similar acceptors, which vary only in the degree of crystallinity, present such different behaviors with varying P3HT $M_w$ suggests that exploring the $M_w$ dependence on NFA device performance should be conducted on a case-by-case basis.

6. Experimental Section

6.1 Materials
P3HT batches were purchased from Ossila and BASF, or synthesized according to literature procedure. O-IDTBR and EH-IDTBR were synthesized according to literature procedure. All other chemicals were purchased from Sigma Aldrich and used as received.

6.2 Device Fabrication and Characterization

Bulk heterojunction solar cells were fabricated in an inverted architecture (glass/ITO/ZnO/P3HT:IDTBR/MoO3/Ag). Glass substrates, pre-patterned with ITO (15 Ω sheet resistance per square), were cleaned by sonication in acetone, detergent, deionized water and isopropanol before ozone plasma treatment for 10 min. A layer of ZnO, approximately 30 nm, (from Zn(OAc)2 in monoethanolamine (60 µL) and 2-methoxyethanol (2 mL)) was deposited by spin-coating onto the ITO substrate at 4,000 r.p.m. for 40 s, followed by annealing at 150 °C for 20 min. Active layer solutions (P3HT:IDTBR, weight ratio 1:1) were prepared from CB with a total concentration of 24 mg mL\(^{-1}\). The solutions were heated to 70 °C overnight, and the active layer was deposited by spincoating at 2,500 r.p.m. for 1 min. The active layers were then annealed at 125 °C for 12 min, under an inert atmosphere. A MoO3 anode interlayer (10 nm) and Ag anode (100 nm) were then deposited by thermal evaporation through a shadow mask, giving an active area of 0.045 cm\(^2\) per device. The J-V characteristics were measured under AM1.5G (100 mW cm\(^{-2}\)) irradiation using an Oriel Instruments Xenon lamp calibrated to a Si reference cell to correct for spectral mismatch, and a Keithley 2400 source meter.

Electroluminescence (EL) experiments consisted of injecting current from the anode, then collecting the emitted photons as function of wavelength/energy. The injection current, normally 10-30 mA, was provided from a constant flow source by Keithley 2400. The emission spectrum was then collected by a Shamrock 303 spectrograph with an iDUS InGaAs array detector cooled to -90 °C. The obtained EL spectra intensity was calibrated with the spectrum from a calibrated halogen lamp. Photoluminescence (PL) measurements were
carried out by illuminating the device under a 473 nm laser beam, normally keeping it under open circuit condition, in which case we can normally only see excitonic state emission. These measurements used the same detector as EL measurements, mentioned above, to collect the emission spectrum from the cell. The external quantum efficiency (EQE) was measured using a whole spectrum (300 to 1100 nm) of monochromatic light generated by the CVI DIGIKROM 240 type grating spectrometer combined with a tungsten halogen light source. A chopper with a frequency of ~80 Hz was used for reducing the noise of the monochromatic light from the ambient, the light beam coming from the chopper was split into two equal intensity light beam, one for the silicon photodiode and one for the device, and the photocurrent of both of the silicon and the device were detected at the same time, using a Stanford Research Systems SR380 lock-in amplifier, which provides an in-situ calibration. Long pass filters (610, 715, 780, 850, and 1000 nm) were used to filter out the scattered light from the monochromator.

The home-built Time Delayed Collection Field (TDCF) setup uses the second harmonic (532 nm) of an actively Q-switched sub-ns Nd:YVO₄ laser (INNOLAS picolo AOT) operating at 5 kHz as excitation. To minimize the RC response time, a small device area of 1 mm² is used. The samples were measured under dynamic vacuum conditions to avoid any degradation. The 532 nm laser beam was tightly focused on the sample. A Keysight S1160A functional generator was used to provide the pre-bias and extraction bias, while a Keysight four channel digital oscilloscope was used to measure the current response of the device. Time delayed collection field measurements were conducted to investigate the field dependence of charge generation. Briefly, the devices were photoexcited with a ns laser pulse during application of a ns pre-bias, which was varied from -2 to 0.75 V, ranging from negative up to open circuit voltage. A high negative collection bias of -4 V was applied after a selected delay time of 10 ns to ensure extraction of separated carriers prior to nongeminate recombination. Furthermore, a low excitation fluence was applied to ascertain that non-
geminate recombination losses during the time between photogeneration and extraction can be neglected. Under these conditions, the total charge $Q_{\text{tot}}$ is a direct measure of the amount of free charge generated by the excitation laser pulse as a function of the applied prebias.

6.3 Morphological Characterization

Samples for differential scanning calorimetry (DSC) were prepared by drop-casting 150 μL of chlorobenzene solutions (25 mg mL$^{-1}$). The films were scrapped off and ~ 2-3 mg were transferred into hermetic DSC pans, which were sealed with punctured lids. A Mettler Toledo DSC 1 was used; two heating and two cooling cycles were recorded at a 5 °C.min$^{-1}$ rate. The first heating cycles were used to construct the liquidus curves, for which the endotherm endset temperatures were used.

Atomic force microscopy (AFM) scans were carried out using the NEXT II (Roman 2) from NT-MDT on samples in actual device configuration. The scans were carried out on 5 x 5 μm$^2$ surface areas, using tapping mode. Dark-field scanning transmission electron microscopy (DF-STEM) was used to analyze samples by operating an electron microscope of model Titan 80-300 CT from Thermo Fisher Scientific at the accelerating voltage of 300 kV. STEM signals were recorded by using a high-angle annular dark-field (HAADF) detector to generate atomic number (Z) sensitive HAADF-STEM images. Core-loss electron energy-loss spectroscopy (EELS) of the samples was also performed in conjunction with DF-STEM for generating the spectrum imaging (SI) datasets. These datasets were then utilized to generate sulfur (S) and nitrogen (N) elemental maps. It is to be noted that EELS spectrometer was set in such a way that respective S-L23 energy loss edge (165 eV) and N-K energy loss edge (401 eV) of S and N could have been acquired. Moreover, the pixel size of 1.3 nm and electron beam dwell time of 20 ms were set during the acquisition of these datasets. To keep the noise level low in S and N maps because of their less atomic concentrations in films, we employed multiple-linear least square (MLLS) method to generate higher quality elemental maps.
Samples were also analyzed in the cross-section direction to understand both morphology and phase mixing/segregation in the bulk of samples. All the cross-sections (X-section) of blend film (in actual device configuration) were prepared by using Helios G4 dual-beam focused ion beam (DB-FIB) scanning electron microscope (SEM). The prepared specimens were then analyzed with a probe-corrected TEM of model Titan 80-300 ST, also from Thermo Fisher Scientific, by operating it at the accelerating voltage of 300 kV. Like the case of the in-plane samples, X-section specimens were also analyzed with STEM-EELS SI technique. This method allowed us to realize the S and N maps in the thin-film growth direction.

Samples for grazing incidence wide-angle x-ray scattering (GIWAXS) were spun-cast on native oxide Silicon substrates. GIWAXS was performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam line 11-3 using an area detector (Rayonix MAR-225) and incident energy of 12.73 keV. The incidence angle (0.1°) was slightly larger than the critical angle, ensuring that we sampled the full depth of the film. The distance between sample and detector was calibrated using a LaB₆ polycrystalline standard. Raw data was normalized by monitor counts and film thickness, then reduced and analyzed using Igor Pro and Nika data reduction software package.[67]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Structures of the fullerene acceptors and their HOMO and LUMO energies, as measured by cyclic voltammetry.\textsuperscript{[26,31-37]} In the cases of PCBPy and F-PCBM no HOMO and LUMO energies were given but the authors noted that they were similar to PC_{61}BM.\textsuperscript{[35,36]}

Figure 2. Structures of the nonfullerene acceptors and their HOMO and LUMO energies, as measured by cyclic voltammetry.\textsuperscript{[24, 41-43, 47-51]}

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**PC_{61}BM**
- HOMO: -5.80 eV
- LUMO: -3.60 eV

**PC_{71}BM**
- HOMO: n/a
- LUMO: -3.74 eV

**IC_{61}BA**
- HOMO: n/a
- LUMO: -3.74 eV

**IC_{71}BA**
- HOMO: -5.60 eV
- LUMO: -3.70 eV

**PCBPy**
- HOMO: n/a
- LUMO: n/a

**F-PCBM**
- HOMO: n/a
- LUMO: n/a

**PCBDAN**
- HOMO: -5.84 eV
- LUMO: -3.64 eV

**Bis-PDI-8DT-EG**
- R = 2-ethylhexyl
- HOMO: -5.44 eV
- LUMO: -3.84 eV

**DIR-2EH**
- R = 2-ethylhexyl
- HOMO: -5.38 eV
- LUMO: -3.30 eV

**Flu-RH**
- R = n-octyl
- HOMO: -5.58 eV
- LUMO: -3.53 eV

**FBR**
- R = n-octyl
- HOMO: -5.70 eV
- LUMO: -3.57 eV

**O-IDTB**
- R = n-octyl
- HOMO: -5.51 eV
- LUMO: -3.88 eV

**EH-IDTB**
- R = 2-ethylhexyl
- HOMO: -5.58 eV
- LUMO: -3.90 eV

**IDFB**
- R = n-octyl
- HOMO: -5.75 eV
- LUMO: -3.70 eV

**HM**
- R = 2-ethylhexyl
- HOMO: -5.51 eV
- LUMO: -3.84 eV

**BTA1**
- R = n-octyl
- R = n-hexyl
- HOMO: -5.51 eV
- LUMO: -3.55 eV

**BTA4**
- R = n-hexyl
- HOMO: -5.51 eV
- LUMO: -3.78 eV
Table 1. Summary of the properties of each neat batch of P3HT

<table>
<thead>
<tr>
<th>P3HT Batch</th>
<th>M_w [kDa]</th>
<th>M_n [kDa]</th>
<th>PDI</th>
<th>RR [%]a)</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>17</td>
<td>13</td>
<td>1.31</td>
<td>96</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>15</td>
<td>1.34</td>
<td>96</td>
</tr>
<tr>
<td>C</td>
<td>34</td>
<td>26</td>
<td>1.35</td>
<td>95</td>
</tr>
<tr>
<td>D</td>
<td>64</td>
<td>35</td>
<td>1.83</td>
<td>96</td>
</tr>
<tr>
<td>E</td>
<td>94</td>
<td>59</td>
<td>1.59</td>
<td>97</td>
</tr>
</tbody>
</table>

a) measured from 1H NMR with CDCl₃ as the solvent.

Figure 3. a) Structures of P3HT and the IDTBR acceptors, b) box plots of the PCE achieved in P3HT:O-IDTBR devices, with varying polymer M_w, c) box plots of the PCE achieved in P3HT:EH-IDTBR devices, with varying polymer M_w.

Table 2. Summary of the J-V characteristics of inverted architecture P3HT:IDTBR OSCs

<table>
<thead>
<tr>
<th>Active Layer</th>
<th>M_w [kDa]</th>
<th>VOC [V]</th>
<th>JSC [mA cm⁻²]</th>
<th>FF</th>
<th>Max PCE/Average PCEa)</th>
<th>Standard Deviationa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT A:O-IDTBR</td>
<td>17</td>
<td>0.67</td>
<td>11.8</td>
<td>0.50</td>
<td>4.0/3.6</td>
<td>0.24</td>
</tr>
<tr>
<td>P3HT B:O-IDTBR</td>
<td>20</td>
<td>0.74</td>
<td>12.0</td>
<td>0.61</td>
<td>5.4/4.7</td>
<td>0.38</td>
</tr>
<tr>
<td>P3HT C:O-IDTBR</td>
<td>34</td>
<td>0.73</td>
<td>14.6</td>
<td>0.66</td>
<td>7.0/6.7</td>
<td>0.23</td>
</tr>
<tr>
<td>P3HT D:O-IDTBR</td>
<td>64</td>
<td>0.74</td>
<td>13.1</td>
<td>0.62</td>
<td>6.0/5.7</td>
<td>0.22</td>
</tr>
<tr>
<td>P3HT E:O-IDTBR</td>
<td>94</td>
<td>0.74</td>
<td>12.1</td>
<td>0.62</td>
<td>5.5/5.3</td>
<td>0.13</td>
</tr>
<tr>
<td>P3HT A:EH-IDTBR</td>
<td>17</td>
<td>0.79</td>
<td>12.0</td>
<td>0.65</td>
<td>6.3/5.9</td>
<td>0.34</td>
</tr>
<tr>
<td>P3HT B:EH-IDTBR</td>
<td>20</td>
<td>0.77</td>
<td>12.6</td>
<td>0.69</td>
<td>6.3/6.0</td>
<td>0.24</td>
</tr>
<tr>
<td>P3HT C:EH-IDTBR</td>
<td>34</td>
<td>0.77</td>
<td>12.0</td>
<td>0.68</td>
<td>6.1/5.9</td>
<td>0.28</td>
</tr>
<tr>
<td>P3HT D:EH-IDTBR</td>
<td>64</td>
<td>0.78</td>
<td>11.3</td>
<td>0.69</td>
<td>6.2/5.9</td>
<td>0.18</td>
</tr>
<tr>
<td>P3HT E:EH-IDTBR</td>
<td>94</td>
<td>0.78</td>
<td>11.7</td>
<td>0.68</td>
<td>6.2/5.9</td>
<td>0.20</td>
</tr>
</tbody>
</table>

a) average PCE and standard deviation were calculated over 8 devices

Figure 4. (a) Normalized photoluminescence spectrum (at open circuit condition) and (b) Normalized electroluminescence spectrum with 30 mA injection current density for P3HT:O-IDTBR devices, with varying P3HT M_w
**Figure 5.** (a) Extended external quantum efficiency and electroluminescence; (b) Voltage losses comparisons with respect to varying P3HT Mw in P3HT:O-IDTBR devices.

**Table 3.** Summarized voltage losses for different Mw P3HT:O-IDTBR devices

<table>
<thead>
<tr>
<th>Mw [kDa]</th>
<th>E_g [eV]</th>
<th>V Oc,SQ [V]</th>
<th>V Oc,rad [V]</th>
<th>ΔV Oc,abs [V]</th>
<th>V Oc [V]</th>
<th>ΔV Oc,nrad [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1.55</td>
<td>1.28</td>
<td>1.18</td>
<td>0.10</td>
<td>0.66</td>
<td>0.52</td>
</tr>
<tr>
<td>20</td>
<td>1.55</td>
<td>1.28</td>
<td>1.16</td>
<td>0.12</td>
<td>0.74</td>
<td>0.42</td>
</tr>
<tr>
<td>34</td>
<td>1.55</td>
<td>1.28</td>
<td>1.13</td>
<td>0.15</td>
<td>0.74</td>
<td>0.39</td>
</tr>
<tr>
<td>64</td>
<td>1.55</td>
<td>1.28</td>
<td>1.17</td>
<td>0.11</td>
<td>0.75</td>
<td>0.42</td>
</tr>
<tr>
<td>94</td>
<td>1.55</td>
<td>1.28</td>
<td>1.16</td>
<td>0.12</td>
<td>0.76</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Figure 6.** The total amount of charge (Q_{tot}) extracted from the device in a TDCF experiment as a function of the applied prebias during photoexcitation superimposed on the JV-curve of the respective device for a) P3HT-E:O-IDTBR (blue), b) P3HT-C:O-IDTBR (red), and c) P3HT-A:O-IDTBR (green).
Figure 7. Phase diagrams of different molecular weight P3HTs and (EH-) and O-IDTBR binaries obtained on the basis of the DSC thermograms. The endset of the melting transition at each composition was used. a) P3HT: EH-IDTBR, 20 kDa (red) 34 kDa (blue) and 94 kDa (grey) the eutectic point relative to the EH-IDTBR is located at 0.5 for P3HT 20 kDa and 94 kDa, b) P3HT: O-IDTBR 20 kDa (red), 34 kDa (blue), 64 kDa (green) and 94 kDa (grey).
Figure 8. a) AFM images of P3HT:O-IDTBR blends with varying polymer Mw (17 kDa, 34 kDa, 64 kDa and 94 kDa), b) in-plane HDAAF-STEM images, with elemental sulfur (red) and nitrogen (green) mapping, of P3HT:O-IDTBR blends with varying polymer Mw (17 kDa, 34 kDa, 64 kDa and 94 kDa).
P3HT remains among the only scalable donor polymers to be used successfully in photovoltaics. In combination with fullerene acceptors it has been able to achieve a PCE of 7.4%, a value that has since been exceeded with the use of non-fullerene acceptors. In this work, the dependence of P3HT molecular weight on device performance has been investigated using two non-fullerene acceptors with differing crystallinities.

**Keywords:** organic photovoltaics, poly (3-hexylthiophene), nonfullerene, molecular weight, IDTBR


**Progress in poly (3-hexylthiophene) organic solar cells and the influence of its molecular weight on device performance**
Supporting Information

Progress in poly (3-hexylthiophene) organic solar cells and the influence of its molecular weight on device performance


Figure S1. a) Box plots of the photocurrent (JSC) of P3HT:O-IDTBR devices, with varying Mw, b) box plots of the open circuit voltage (VOC) of P3HT:O-IDTBR devices, with varying Mw, c) box plots of the fill factor (FF) of P3HT:O-IDTBR devices, with varying Mw, d) box plots of the photocurrent (JSC) of P3HT:EH-IDTBR devices, with varying Mw, e) box plots of the open circuit voltage (VOC) of P3HT:EH-IDTBR devices, with varying Mw, f) box plots of the fill factor (FF) of P3HT:EH-IDTBR devices, with varying Mw.
**Figure S2.** Differential Scanning Calorimetry (DSC) endotherms of the heating cycle of P3HT-B:O-IDTBR blends, the y-axis has the units of mW, and the traces have been offset for clarity.

**Figure S3.** DSC endotherms of the heating cycle of P3HT-C:O-IDTBR blends, the y-axis has the units of mW, and the traces have been offset for clarity.

**Figure S4.** DSC endotherms of the heating cycle of P3HT-D:O-IDTBR blends, the y-axis has the units of mW, and the traces have been offset for clarity.
Figure S5. DSC endotherms of the heating cycle of P3HT-E:O-IDTBR blends, the y-axis has the units of mW, and the traces have been offset for clarity.

Figure S6. DSC endotherms of the heating cycle of P3HT-B:EH-IDTBR blends, the y-axis has the units of mW, and the traces have been offset for clarity.

Figure S7. DSC endotherms of the heating cycle of P3HT-C:EH-IDTBR blends, the y-axis has the units of mW, and the traces have been offset for clarity.
**Figure S8.** DSC endotherms of the heating cycle of P3HT-E:EH-IDTBR blends, the y-axis has the units of mW, and the traces have been offset for clarity.

![DSC endotherms](image)

**Figure S9.** High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the in-plane view of a) the P3HT-A:O-IDTBR blend, b) the P3HT-C:O-IDTBR blend, c) the P3HT-D:O-IDTBR blend and d) the P3HT-E:O-IDTBR blend.

![HAADF-STEM in-plane images](image)

**Figure S10.** HAADF-STEM images of the cross-section view of a) the P3HT-A:O-IDTBR blend, b) the P3HT-C:O-IDTBR blend, c) the P3HT-D:O-IDTBR blend and d) the P3HT-E:O-IDTBR blend.

![HAADF-STEM cross-section images](image)
Figure S11. HDAAF-STEM images, with elemental sulfur (red) and nitrogen (green) mapping, of the cross-section view of a) the P3HT-A:O-IDTBR blend, b) the P3HT-C:O-IDTBR blend, c) the P3HT-D:O-IDTBR blend and d) the P3HT-E:O-IDTBR blend.

Figure S12. Grazing-incidence wide-angle x-ray scattering (GIWAXS) linecuts of a) the in-plane (Q_xy) and b) the out-of-plane (Q_z) direction for P3HT:O-IDTBR blends.

Figure S13. GIWAXS linecuts of a) the in-plane (Q_xy) and b) the out-of-plane (Q_z) direction for P3HT:EH-IDTBR blends.
**Figure S14.** Schematic depiction of the balance between phase separation and percolation pathways in polymer:acceptor blends. Purple represents pure NFA, dark red represents pure P3HT, red represents P3HT-rich amorphous phase, blue represents NFA-rich amorphous phase.