

The resurgence of Organic Photovoltaics

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Abstract:

Several advances were reported in the field of organic photovoltaics in the last two years. Development and application of non-fullerene acceptors in particular has injected new life into the field. Exploitation of such materials in ternary blends and tandem solar cell structures has in fact enabled record high efficiencies >15%, thus paving the way towards commercialisation.

Introduction:

Organic semiconductors (OS) rapidly became a success story for light-emitting diodes and then displays, now found in a plethora of commercial applications with further current focus on extending their performance in the near infra-red [1,2]. On the other hand, organic photovoltaics (OPVs) have lagged behind due to their limited efficiencies. Recently, advances in OPV research led to the fabrication of record high 17.3% [3••] efficient solar cells, thus demonstrating a potentially bright future for OPVs as well. The key competitive advantage of OPVs is their solution-processability which can offer low-cost fabrication of flexible devices over large areas [4]. They can also be semi-transparent, and therefore penetrate into niche markets such as photovoltaic windows [5,6]. Indeed, OPVs have already shown excellent potential especially for wearable technologies and indoor energy generation [7,8].

In the period 1980 to 2010 several milestones led to the increase of power conversion efficiencies (PCE) of OPVs from under 1% to approximately 10% [9] (stated PCE values in this review refer to measurements taken under the typical AM 1.5G solar standard). First was the introduction of the bilayer structure [10]. Forming a heterojunction between electron donating (donor) and electron accepting (acceptor) OSs, allowed for efficient charge separation by providing a driving force to overcome the relatively high binding energy of excitons in OS (~ 0.5 eV). The advent of the bulk heterojunction (BHJ) concept that followed, allowed then formation of extended donor-acceptor interfaces and higher performance [11,12]. Fullerenes, and especially the soluble derivatives PC₆₁BM and PC₇₁BM, quickly became the "elective" acceptors mainly due to their ability to form effective BHJs [13] (see Figure 1 for the chemical structures of all reported materials). In the years 2000 – 2010 the efforts of the scientific community were directed to the careful optimisation of the morphology of active layers via additives and annealing, the development of interlayers to enhance charge transport to the electrodes (and extraction from these) and, most importantly, the synthesis of high-mobility and strongly absorbing donors [14]–[21]. Crucially, efforts in the last few years have included the development of non-fullerene acceptors (NFAs).

In this review we initially discuss advantages and limitations of single-junction OPVs based on fullerene acceptors, and then map out how developments in NFAs along with the effective use of the concepts of ternary blends and tandem cells allowed for a major enhancement in the performance of OPVs in the last two years.

Fullerene acceptors:

The dominance of fullerene utilisation in OPVs stems from their ability to form BHJ interpenetrating networks of good quality and their relatively high electron mobilities ($\sim 1 \times 10^{-2}$ cm²/Vs) [13]. On the other hand, fullerenes suffer from relatively limited tunability of electron affinities [22], which in turn limits the number of potential donor materials that can be utilised and more importantly exhibit weak absorption in the visible and near infra-red regions, thus effectively limiting the maximum value of short circuit current densities (J_{sc}). Furthermore, although there is evidence that the crystallinity of the fullerene phase influences OPV performance this lacks optimisation since the crystal phase depends on the solvent and is difficult to characterise [23,24]. These drawbacks restricted attainment of efficiencies above 15% for single junction OPVs based on donor:fullerene blends. Only recently has the crystal structure of solvent-free PC₆₁BM single crystals been resolved and the morphological and optical properties of these crystals characterised [25]–[27•]. These studies can offer a pathway towards optimisation of fullerenes whose utilisation is likely to persist especially in ternary blends.

Non- fullerene acceptors:

The development of NFAs has become a topic of intense study as researchers are struggling to overcome fullerene challenges. In NFAs, energy levels and absorption spectra can be tuned more easily than in the case of fullerenes so as to optimise device function. The most widely studied classes of NFAs are perylene diimides (PDIs) and fused-ring electron acceptors (FREAs) [28]. PDIs have been functionalised for use in BHJs in the positions shown in

Figure 1d. Indeed the frontier energy levels (especially the lowest unoccupied molecular orbital (LUMO)) of NFAs are shown to be readily tuneable and to depend on the units attached to these positions. For example, Hartnett et al. [29] functionalised the ortho positions of the PDIs with the addition of hexyl groups (hexyl-PDI) and phenyl groups (phenyl-PDI). As expected, the different modifications led to different LUMO levels (3.83 eV and 4.01 eV for hexyl-PDI and phenyl-PDI respectively) and energy gaps. Blending with PBT13T resulted in a PCE of 3.6% for phenyl-PDI and 0.6% for hexyl-PDI. This significant discrepancy was attributed to the different morphologies of the blends. Transmission electron microscopy (TEM) revealed features ~100 nm in length in PBT13T:hexyl-PDI blends, thus suggesting poor mixing whereas PBT13T:Phenyl-PDI blends showed homogeneous and well-mixed regions. These results exemplify a challenge in NFAs. Although the strong π - π stacking in these systems leads to high mobilities ($\sim 0.2 \times 10^{-2} \text{ cm}^2/\text{Vs}$) [30], formation of micrometre-sized crystallites is observed which significantly hinders performance in BHJs.

The best performing NFAs are FREAs which consist of two strongly π -electron-withdrawing moieties linked by a planar π bridge consisting of fused rings [31]. As expected, core size and the choice of end group significantly affect the optical and electrochemical properties of FREAs. To limit the formation of large domains of NFAs via π - π stacking, the fused rings are substituted with side chains that project above or below the plane. The added bonus is that these side chains can also be used to tailor solubility, mobility, and active-layer morphology [30].

A very successful FREA is ITIC (Figure 1h) [32] developed by end capping IT with a so called INCN moiety. INCN features one carbonyl and two cyano groups that downshift LUMO levels thanks to their electron-withdrawing character. The four (rigid) hexylphenyl groups helped to form PTB7-Th:ITIC blends that had nearly uniform crystalline grains (~10 nm), resulting in PCEs ~6.8%. When Haijun et al. [33•] blended ITIC with a donor with complementary absorption spectrum (J71 - Figure 1p), they increased the PCE to 11.4%, and the J_{sc} from 14.3 to 17.32 mA/cm². Incident photon to current efficiency measurements of devices based on J71:ITIC blends showed broad and efficient photo-response from 300 to 790 nm, indicating high photo-conversion efficiency for the absorptions of both J71 and ITIC. Transient absorption measurements also confirmed that hole transfer takes place at pump wavelengths where only ITIC is excited. These results show that charge transfer from excited states formed both in the donor and the acceptor can occur effectively in NFA blends, leading to higher J_{sc} with respect to fullerene-based blends [33•, 34]. These findings are particularly interesting since they provide design rules for NFA OPV systems. Further PCE enhancements were achieved by Zhao et al. [35•] by performing fluorination of ITIC as shown in Figure 1i (IT-4F). By exploiting the enhanced absorption and reduced energy gap of IT-4F, they obtained a 13.1% efficiency for single junction OPVs using PBDB-T-SF as donor. Another noteworthy example of a NFA is COi8DFIC [36•]. This low bandgap NFA (1.26 eV) exhibited an outstanding J_{sc} of 26.12 mA/cm² with a 12.16% PCE in PTB7-Th:COi8DFIC blends. This impressive result was attributed to the complementary absorption and well-balanced mobilities of PTB7-Th and COi8DFIC ($\sim 10^{-4} \text{ cm}^2/\text{Vs}$).

Overall, a variety of advances in NFAs since 2015 increased OPV PCEs from 6% to 13%. Electron affinities can be effectively tailored over a very wide range of structures and the knowledge and techniques that have been previously applied to donors can be exploited [37]. Large, medium, and small energy gap NFAs are now available and can accommodate essentially all types of donors to achieve complementary spectral features. This allows high J_{sc} and PCEs to be attained. However, it is not yet clear that interpenetration of donor and acceptor moieties in NFA BHJs is as good as in the case of fullerene BHJs. Effectively tackling this challenge to ensure the formation of effective BHJs is very likely to lead to even greater improvements in OPVs incorporating NFAs.

Ternary blends and tandem solar cells

The concepts of ternary blends and tandem/multiple solar cells are now widely applied to photovoltaics to counter thermalisation losses. These concepts are particularly useful for OPVs as well, as the coverage of the solar irradiation spectrum is not optimal in single junction donor:acceptor BHJs due to the relatively narrow optical absorption of OS when compared to silicon for example.

Lu et al. [38•] were among the first to combine fullerenes and NFAs in ternary blends [39,40]. This innovative approach partially eliminates the deficiencies of these two types of acceptors by capitalising on their complementary advantages. In their study [38•], PPBDTBT was used as a donor, with ITIC and PC₇₁BM used as acceptors. To enable comparison, devices of binary blends containing only a single acceptor were fabricated as well. The external quantum efficiency spectra of the ternary device had a similar profile to ITIC-only devices with enhanced values in every region of the spectrum. This indicated that whilst most absorption was resulting from ITIC and the donor, photogenerated excitons were dissociated and collected more effectively in the ternary blend. Furthermore, the ternary device was 35% and 43% more efficient than the binary devices of NFAs and fullerenes respectively. Increasing the weight percentage of fullerene content in the ternary blend increased the fill factor as well. A maximum J_{sc} was reached at 40% PC₇₁BM weight concentration, with a corresponding PCE = 10.4%. Interestingly, these results clearly demonstrated that the NFA enhances light absorption in these systems, while the fullerene improves the morphology and charge-carrier transport [38•]. The synergistic use of non-fullerene and fullerene acceptors in ternary blends was also explored by Zhao et al. [41] and Xiao et al. [42•] to boost the PCE. They achieved 12.2% and 14% PCEs respectively. Xiao et al. used a blend of PTB7-Th, COi8DFIC and PC₇₁BM thus obtaining an impressive 28.20 mA/cm² J_{sc} and a 71% fill factor.

Ternary blends have also been used effectively in tandem structures [3•,43] which are particularly useful for OPVs, because OS generally have low mobilities and require active layers of limited thickness compared to inorganic semiconductors [44].

The most successful tandem OPVs to date have been demonstrated by Meng et al. [3•]. In their study, material selection was guided by a semi-empirical analysis from which several desired parameters for an optimised system were extracted. For example, the optimal absorption onsets of the rear and front sub-cells were calculated to be 1050-1150 nm and 720 nm respectively. For their experimental investigations they chose a rear cell constructed by the ternary blend: PTB7-Th, COi8DFIC, PC₇₁BM and a PBDB-T: F-M blend front cell to match the criteria. They also employed computational simulations to determine the optimised active layer thickness. The ensuing strategy enabled fabrication of solution-processed devices with PCEs up to 17.3%, currently the state-of-the-art. This outstanding result stresses the importance of using computational models to guide experimental attempts and more importantly revives interest in the exciting field of OPVs.

The path to commercialisation:

PCEs >15% in fully solution-processed devices, prove OPVs promise as a viable technology for commercialisation. Currently, the biggest obstacle is lack of long-term stability. Although most recent devices containing NFAs report improved stabilities, a deeper understanding is required to elucidate stability to oxygen, moisture, heat, irradiation and mechanical stress [45,46]. For OPVs to fulfil their potential they must also compete with currently growing and established photovoltaic technologies. As lead-free devices, OPVs have an inherent competitive advantage over lead-halide perovskites [47] despite affording lower PCEs. Competition from silicon and copper indium gallium selenide (CIGS) solar cells is possibly even stronger. Although OPVs can be solution-processed, thus offering potentially lower fabrication costs, these established solar technologies already benefit from economies of scale (especially silicon). However, OPVs tend to perform better under indoor illumination conditions [48] and can be flexible. The growing interest in applications where these properties are required can offer a window of opportunities for commercialisation of OPVs. The better integration of computational simulations and experimental techniques seems to be a very fruitful avenue to pursue and will likely play a major role in the future development of OPVs to mitigate challenges in both non-fullerene and fullerene acceptor devices.[49]

Conclusion:

In the last two years we have witnessed significant developments in the field of organic photovoltaics. Better understanding and application of design rules for non-fullerene acceptors has led to an increase in the power conversion efficiency of single junction organic photovoltaics that employ them by a factor of 2. Great strides have also been made in ternary blends by the innovative approach of effectively combining fullerene and non-fullerene acceptors. The 15% power conversion efficiency benchmark has been surpassed in tandem structures by bringing together guidance from computational models and these ternary blends containing the state-of-the-art non-fullerene acceptors. With the revived interest in organic photovoltaics that these advances bring, we can expect attainment of even higher efficiencies as well as the development of strategies to mitigate issues with stability of organic photovoltaics in the near future.

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Declaration of interest: None

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- of special interest
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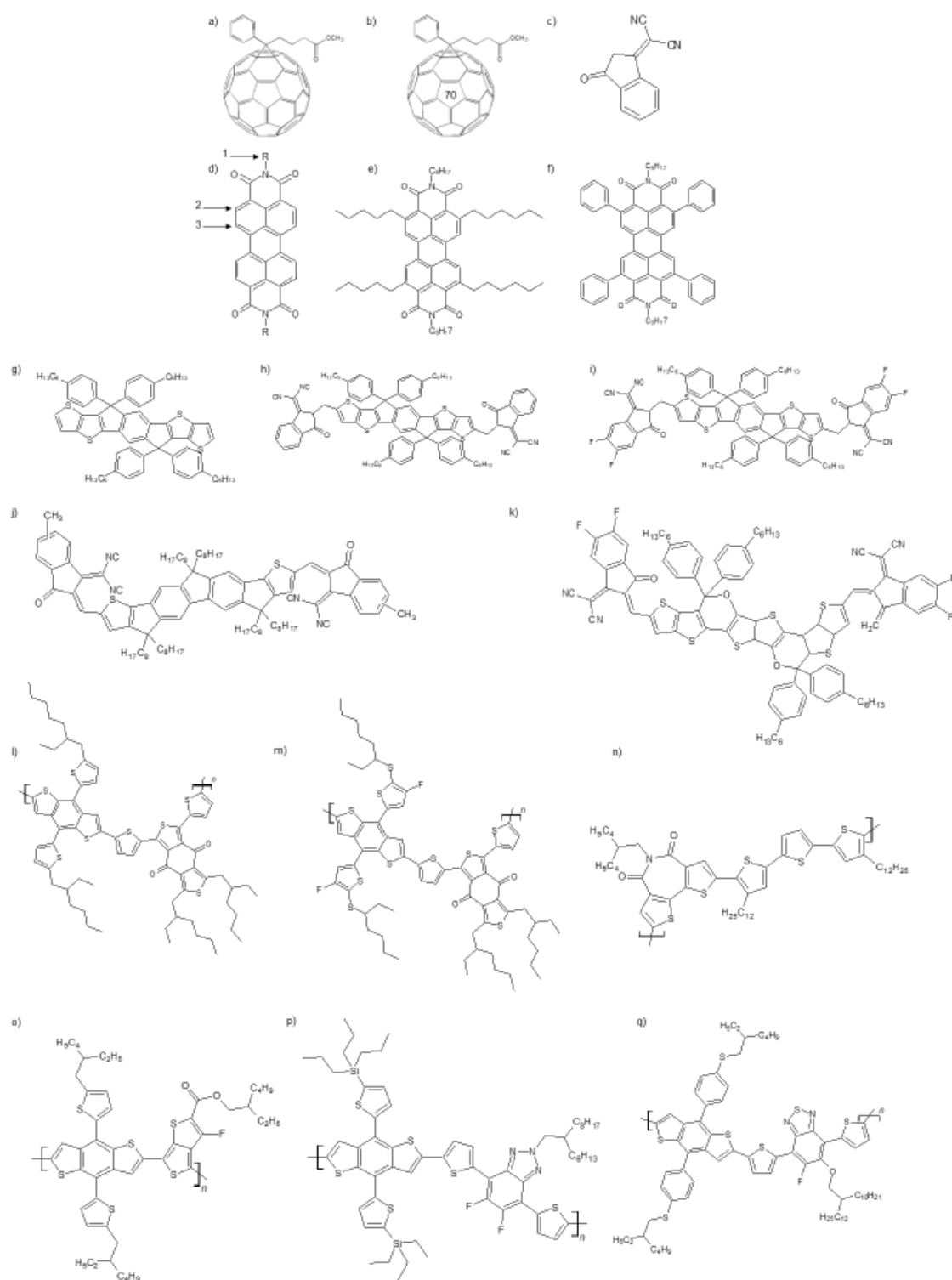


Figure 1: Reported chemical structures: a) $PC_{61}BM$, b) $PC_{71}BM$, c) $INCN$ d) PDI (1. imide functionalisation, 2. ortho functionalisation 3. bay functionalisation), e) Hexyl-PDI, f) Phenyl-PDI, g) IT, h) ITIC, i) IT-4F, j) F-M, k) $COi8DFIC$, l) $PBDB-T$, m) $PBDB-T-SF$, n) $PBTi3T$, o) $PTB7-TH$, p) $J71$, q) $PPBDTBT$.