The physics of small molecule acceptors for efficient and stable bulk-heterojunction solar cells

Nicola Gasparini^{1,2*}, Andrew Wadsworth,³ Maximilian Moser,³ Derya Baran², Iain McCulloch^{2,3} and Christoph J. Brabec^{1,4*}

¹Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany

²Physical Sciences and Engineering Division, KAUST Solar Center (KSC), King Abdullah University of Science and Technology (KAUST), KSC Thuwal 23955-6900, Saudi Arabia.

³Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, SW7 2AZ, UK

⁴Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstrasse 2a, 91058 Erlangen, Germany

ABSTRACT

Organic bulk heterojunction solar cells based on small molecule acceptors have recently seen a rapid rise in the power conversion efficiency with values exceeding 13%. This impressive achievement is obtained by simultaneous reduction of voltage and charge recombination losses within this class of materials as compared to fullerene-based solar cells. In this contribution, we review the current understanding of the relevant photo-physical processes in highly efficient non-fullerene acceptor (NFA) small molecules. Charge generation, recombination and charge transport is discussed in comparison to fullerenes based composites. Finally, we review the superior light and thermal stability of nonfullerene small molecular acceptor based solar cells and highlight the importance that NFA based composites enable devices without early performance loss, thus resembling so-called burn-in free devices.

1. Introduction

The field of organic solar cells is nowadays facing a new era, ferried by the development of novel and stable acceptor materials,^[1–20] the so called non fullerene acceptors (NFAs), making the 15% power conversion efficiency (PCE) threshold not anymore a research dream but a real goal.^[21] Despite the priority of high efficiency, the device longevity as well as the large area fabrication need to be addressed to make competitive organic solar cells with the other thin-film photovoltaic technologies.^{[22][23]} For decades fullerene derivatives, e.g. PCBM and PC₇₀BM, were the common acceptor materials used in combination with the donor small molecules or polymers to form the photoactive layer of bulk heterojunction (BHJ) solar cells.^[24] These fullerene acceptors derivate from C₆₀ and C₇₀ have dominated the OPV landscape due to their advantageous properties like a high electron mobility, strong acceptor properties to most donor materials due a low lying energy level, efficient charge separation with internal quantum efficiencies approaching unity as well as excellent photo-stability.^[25] Nevertheless, fullerene-based acceptors present limitations such as i) the weak absorption in the visible range, which limits the ability of light-to-current conversion,^[26] ii) the limited tunability of the frontier orbitals,^[27] iii) the poor stability under light and thermal stress^{[28][29][30]} iv) the high synthetic costs,^[23] and finally, their inherent low miscibility with most organic donors.^[31] These limitations make fullerenes the bottleneck for further improving device efficiency and stability.^{[32][33]} In particular for the latter point, blends with common C₆₀ fullerene acceptors may feature a significant burn-in loss.^{[34][35]} Burn-in is the standard terminology for an early state degradation in semiconductor devices under electrical or temperature stress, which stabilizes after the burn-in period. In organic solar cells, burn-in phenomena dominantly affect the short-circuit current, which was recently explained by the formation of fullerene dimers.^[36] While fullerene oligomerization can be alleviated using, e.g., C₇₀ based fullerenes or higher fullerene adducts, fullerene-based blends without burn-in are rare exceptions.^[37] As such, replacing the fullerene acceptor by non-fullerene molecules constitutes one promising path

towards organic solar cells with improved long-term operational stability.^{[38][39][40]} A unifying parameter of different PV technologies is the PCE, defined as the ratio of output energy from the solar cell to the input energy from the sun. The power output is defined by the three photovoltaic parameters: short-circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF). Despite the several attempts that have been made in fullerene-based devices to overcome the low light harvesting and transport limitation of the active layer, to tackle J_{sc} and FF, respectively, such as ternary^{[41][42]} and tandem^{[43][44]} configurations, the obstacle of the high voltage losses in donor:PCBM blends has yet to be overcome.^{[45][46]} The voltage losses of organic solar cells, defined as the difference of the bandgap (E_g) of the absorber materials and the open circuit voltage (V_{oc}) of the device at 1 sun illumination are arising from: i) the large non-radiative recombination loss in OPV, denoted by the extremely low quantum efficiency of electroluminescence (EQE_{EL}), typically in the 10^{-6} - 10^{-9} range, which is significantly lower compared to Silicon and perovskite technology (10^{-2} - 10^{-4}); ii) the offset between the bandgap of the blend and the energy of the charge transfer state (E_g-E_{CT}), the driving force of charge separation in the BHJ devices.^{[47][48][49][50]} Historically, research efforts have been directed towards reducing the voltage losses while maintaining the same time high external quantum efficiency, however, no donor:fullerene combinations simultaneously deployed minimized energetic offset losses (E_{CT}), high EQE_{EL} ($>10^{-4}$) with suppressed recombination losses (<300 mV) along with high fill factor (FF) values. Encouragingly, non-fullerene small molecules acceptors (NFA) are particularly attractive because of:

- 1) the possibility of extending the absorption window of high and mid band gap donors through high absorption coefficients in the near-infrared (NIR) by chemical design, allowing the spectral sensitivity of organic solar cells to be extended.^{[13][14][51][52][1][53][54]}
- 2) the ability of improving charge separation despite negligible driving force, defined as the offset between the bandgap (E_{gap}) of the donor/acceptor materials and the energy of the charge transfer (CT) state (E_{CT}), which is typically greater than 0.3eV.^{[55][56]}

- 3) the capability of reducing charge recombination channels, leading to solar cells with extremely low recombination rates.^{[57][40]}
- 4) the replacement of fullerene derivatives increases the photo-stability allowing burn-in free devices.^[38]

As a result, PCEs over 13% have been achieved with medium band gap polymers along with extended lifetimes and operative stability over 2000h.^{[38][21]} Among the strategies being developed for NFA, the most popular is to synthesize A-A-D-A-A (acceptor-acceptor-donor-acceptor-acceptor) planar molecular structures, like IDTBR or A-D-A (acceptor-donor-acceptor) like ITIC.^{[1][3]} In fact, the strong electron-withdrawing units exposed at the two sides of the backbone improved the molecular contacts, allowing efficient intermolecular charge transport. Moreover, the planar and rigid configuration enhanced the molecular packing, thus, increasing the electron mobility.

In this article we review the recent progress in small molecular non fullerene acceptor based solar cells. In the first part we discuss the physics of NFAs by focusing onto the reduced voltage losses as well as the charge recombination with respect to fullerene-based systems. In the second part we analyze the operational stability of non fullerene based systems under light and thermal stress compared to PCBM based devices and find an excitingly high photo-stability of these composites with various donors.

2. Photophysics of small molecule acceptor based solar cells

2.1. Reduced Voltage loss

As aforementioned, NFAs based solar cells are delivering V_{oc} as high as 1.2V due to the simultaneous effects of higher lowest unoccupied energy level (LUMO) compared to PCBM and reduced voltage losses.^[58] To get insight into the latter parameter it is important to recall

the detailed balance theory,^[48] valid for any PV technology, in which the voltage loss in solar cells is depending on the three factors of equation 1:

$$q\Delta V = E_g - qV_{oc} = (E_g - qV_{oc}^{SQ}) + q\Delta V_{oc}^{rad} + q\Delta V_{oc}^{non-rad} \quad (1)$$

where q is the elementary charge, ΔV is the voltage loss, V_{oc}^{SQ} is the maximum achievable voltage according to the Shockley-Queisser limit, assuming a step-function external quantum efficiency (EQE), ΔV_{oc}^{rad} is the radiative recombination affecting the voltage loss below the bandgap and $\Delta V_{oc}^{non-rad}$ is the non-radiative recombination loss. For a more detailed explanation on the theory see Rau et al.^[48]

Unfortunately, the first term of equation 1 ($E_g - qV_{oc}^{SQ}$) is unavoidable for any type of solar cells since it is due to radiative recombination processes happening above the bandgap. This loss is typically between 0.25 eV and 0.30 eV.^[59]

The second term, $q\Delta V_{oc}^{rad}$ reflects the additional losses happening below the bandgap. This term is negligible for inorganic and perovskite based devices since they depict a steep absorption edge. Differently, as described by Vandewal et al., fullerene-based solar cells,^[60] show usually very high ΔV_{oc}^{rad} due to the existence of CT states, red shifted (lower energy) than the bandgap of the absorber. Benchmark polymer blends, such as P3HT:PCBM and PTB7:PC₇₀BM feature ΔV_{oc}^{rad} between 0.2 V and 0.7 V.^[56]

Finally, the third term, $\Delta V_{oc}^{non-rad}$ reflects non-radiative recombination processes. By calculating the electroluminescence quantum efficiency (EQE_{EL}) of the device it is possible to estimate this loss according to equation 2:

$$\Delta V_{oc}^{non-rad} = -\frac{kT}{q} \ln(EQE_{EL}) \quad (2)$$

where k is the Boltzmann constant and T is the temperature. Clearly, in order to minimize $\Delta V_{oc}^{non-rad}$ the EQE_{EL} should be maximized. Compared to the inorganic counterparts (Si and perovskite) in which $\Delta V_{oc}^{non-rad}$ is about 0.25V or lower, fullerene-based organic devices show

much larger non-radiative losses, typically around 0.38-0.44V, translated in EQE_{EL} values in the order of 10^{-6} - 10^{-8} . By replacing fullerenes with NFAs, the second and third term of equation 1 can be addressed and as we will review in the next section, reduced ΔV_{oc}^{rad} and $\Delta V_{oc}^{non-rad}$ can be achieved, leading to solar devices with voltage losses lower than 0.3V.

Recently, Vandewal et al., reported a large set of donor-fullerene blends, both solution processed and thermal evaporated, featuring energy differences between the ground state and the CT state in the range from 0.7 eV to 1.7 eV.^[61] As depicted in **Figure 1**, they observed a clear correlation between EQE_{EL} and E_{CT} and concluded that $\Delta V_{oc}^{non-rad}$ increases with decreasing E_{CT} . This striking correlation is associated with an increased wave-function overlap between the relaxed CT state and higher order vibrational modes of the ground state.^[56] Moreover, since no differences in $\Delta V_{oc}^{non-rad}$ were observed upon replacement of carbon-hydrogen bond with carbon-deuterium bond, the authors concluded that $\Delta V_{oc}^{non-rad}$ losses are intrinsic to organic materials and conceptually different from other thin film technology, in which non-radiative recombination losses are referred to surface or Auger recombination.^[62]

Figure 1. a) V_{oc} as a function of E_{CT} for a series of donor:fullerene systems reviewed on ref.^[61] The red line shows the ideal V_{oc} , according to Shockley–Queisser (SQ) assumptions, as a function of E_{CT} . b) $\Delta V_{oc}^{non-rad}$ as a function of the E_{CT} calculated from EQE_{PV} (filled symbols) and EQE_{EL} (open symbols). The red dashed line indicates an empirical lower limit of $\Delta V_{oc}^{non-rad}$ as a function of E_{CT} . Reproduced with the permission from Ref.^[61]

Following up this hypothesis of a fundamental correlation between the CT energy and the non-radiative V_{oc} losses, we review donor:NFA blends that surpass these intrinsic non-radiative voltage losses in fullerene-based system, proving insight into different processes governing CT state formation leading to unprecedented low V_{oc} losses for this new class of OPV composites.

Figure 2. Chemical structures of polymers (a) and small molecular acceptors (b) reviewed in this work.

Baran et al.,^[55] studied the origin of the high V_{oc} in Pff4TBT-2DT:FBR blends (V_{oc} =1.12V, PCE=7.8%) compared to Pff4TBT-2DT:PC₇₀BM solar cells (V_{oc} =0.76V, PCE=7.5%). **Figure 2** shows the chemical structures of the polymers and SMA reviewed in this work. The ΔV_{oc}^{rad} for Pff4TBT-2DT:FBR is calculated by measuring the real quantum efficiency using sensitive Fourier transform photocurrent spectroscopy (FTPS) and electroluminescence spectroscopy (EL) as depicted in **Figure 3a**. Interestingly, the NFA blend does not show any CT absorption below the bandgap, meaning that the donor-acceptor interface is not a limiting factor for the V_{oc} loss. The $\Delta V_{oc}^{non-rad}$ are calculated by EL measurements. **Figure 3b** clearly shows that FBR-based solar cells deliver almost 2 orders higher emission compared to Pff4TBT-2DT:PC₇₀BM solar cells, suggesting lower non radiative recombination in the NFA blends. Indeed, Pff4TBT-2DT:FBR delivered the lowest $\Delta V_{oc}^{non-rad}$ of 230 mV compared to Pff4TBT-2DT:PCBM ($\Delta V_{oc}^{non-rad}$ of 330 mV). The losses in the non-fullerene device result in EQE_{EL} in the range of 10^{-3} , a value which is comparable with perovskite devices.

Similar results were also obtained for a novel NFA based on P3TEA:SFPDI solar cells with PCE of 9.5%.^[56] Also in this case the authors found that the absorption onset of the blend almost overlaps with the pure polymer P3TEA (**Figure 4a**). This result suggests that the energy difference between singlet exciton on the donor and/or acceptor spectrally overlaps with the CT states. As a result, ΔV_{oc}^{rad} is estimated to be as low as 0.07 V. To confirm the absence of sub-bandgap absorption, the authors carried out EL measurements on P3TEA:SFPDI blend and pure P3TEA. **Figure 4b** clearly depicts that the two spectra are nearly identical, showing that no CT absorption is detected, consistent with FTPS data. Moreover, the CT states typically feature a Gaussian distribution, while the emission of the NFA based blend showed a vibronic shoulder very similar to the pure polymer. As a result, EQE_{EL} values of 0.5×10^{-4} were calculated both for P3TEA:SFPDI blends as well as for pure P3TEA.

Figure 3. a) The EQE (solid line) determined from EL, the directly measured quantum efficiency (purple line) and FTPS (open circles) used to determine the ΔV_{oc}^{rad} (1.35 V) of the PffBT4T-2DT:FBR device and the voltage loss due to non-radiative recombination ($\Delta V_{oc}^{non-rad}$). b) Comparison of electroluminescence emission spectra of PffBT4T-2DT:PC₇₀BM and PffBT4T-2DT:FBR cells at a given current density. Reproduced with the permission from Ref.^[55]

Figure 4. a) Normalized FTPS spectra of pure P3TEA and blend A-based devices. b) Normalized EL curves of pure P3TEA and blend A-based devices. Reproduced with the permission from Ref.^[56]

Table 1. Photovoltaic parameters and EQE_{EL} of polymer:NFA based devices.

Polymer	NFA	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	EQE_{EL}	ref
Pff4TBT-2DT	FBR	11.5	1.12	0.61	7.80	1x10 ⁻⁴	[51]
	IDTBR	15.0	1.07	0.62	9.95	3x10 ⁻⁵	[51]
	PC ₇₀ BM	16.0	0.76	0.62	7.50	1x10 ⁻⁶	[51]
P3TEA	SFPDI	13.27	1.11	0.64	9.5	0.5x10 ⁻⁴	[52]
PBDB-T	ITIC	16.81	0.90	0.74	11.21	1x10 ⁻⁶	[3]
	PC ₇₀ BM	12.80	0.85	0.68	7.45	-	[3]
	ITIC	17.0	0.89	0.66	10.0	5.8 x10 ⁻⁷	[81]
	C8-ITIC	19.7	0.87	0.73	12.4	1.8 x10 ⁻⁶	[81]
PFBDB-T	ITIC	18.5	0.95	0.66	11.7	4.3 x10 ⁻⁷	[81]
	C8-ITIC	19.6	0.94	0.72	13.2	2.9 x10 ⁻⁶	[81]

The first example of a non-fullerene based system outperforming fullerene blends was reported by Hou et al.^[3] In this work, PBDB-T was blended with ITIC and PC₇₀BM acceptors delivering 11.21% and 7.45%, respectively, together with enhanced V_{oc} up 0.90 V for PBDB-T:ITIC compared to PBDB-T:PC₇₀BM blend (0.85 V).

Figure 5. The FTPS spectra of PBDB-T:PC₇₀BM and PBDB-T:ITIC based devices, respectively; the short dashed curves are the fitting curves with Equation (3) to obtain values for E_{CT} and λ . Reproduced with the permission from Ref.^[3]

Figure 5 shows the FTPS spectra of fullerene and nonfullerene based solar cells. Differently from the previous reports, a weak CT absorption was detected in this ITIC-based blend. The strength of the CT was calculated according to equation 3:

$$EQE(E) \propto \frac{1}{E\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{CT}+\lambda-E)^2}{4\lambda kT}\right) \quad (3)$$

where λ is related to the width of the CT absorbance band, which depends from internal reorganization and/or energetic disorders.^[63] From the fitting of the data of **Figure 5** according to equation 3, the authors found λ of 0.13 eV and 0.30 eV for PBDB-T:ITIC and PBDB-T:PC₇₀BM, respectively, suggesting reduced recombination across the CT state in the NFA system. It is worth to mention that E_{CT} calculated from fitting the experimental data to equation (3) is in excellent agreement with the differences in V_{oc} reported for the two systems with E_{CT} values of 1.50 eV and 1.42 eV for non-fullerene and fullerene based system respectively. Moreover, the authors calculated the energy loss of the two systems considering the difference between the emissive energy of the pristine polymer versus the CT emission of the blend composite. The PBDB-T:ITIC device features negligible energy losses of 0.09 eV (1.59-1.50

eV), whereas PBDB-T:PC₇₀BM blend is calculated as 0.35 eV (1.77-1.42 eV). These results explained the higher V_{oc} in the NFA systems despite its smaller optical bandgap. Finally, according to equation 2, an EQE_{EL} of 1×10^{-6} was calculated for PBDB-T:ITIC. This significantly lower value compared to Pff4TBT-2DT:FBR and P3TEA:SFPDI reflects the more pronounced non-radiative recombination channels present in PBDB-T:ITIC.

The superior properties of indacenodithieno[3,2-b]thiophene based acceptors over fullerenes were recently reported by Heeney et al.^[81] The authors reported a novel NFA, C8-ITIC presenting a red-shift absorption with increased absorptivity compared to ITIC. Solar devices based on PBDB-T and PFBDB-T as polymer and C8-ITIC as acceptor delivered impressive PCE of 11.7% and 13.2%, respectively and V_{oc} of 0.86V and 0.93V, respectively. The lower V_{oc} reported for PFBDB-T is due to the effect of fluorination in lowering the HOMO and LUMO of the donor, thereby reducing the energy offset with the acceptor. Interestingly, FTPS spectra do not show sub-bandgap absorption resulting in negligible ΔV_{oc}^{rad} values. Additionally, the analysis of EL measurements reveal lower $\Delta V_{oc}^{non-rad}$ for PFBDB-T:C8-ITIC blend (0.33 V) compared to PBDB-T:C8-ITIC (0.38 V). Again, the results obtained are comparable with other NFA-based solar cells.

Although the reason of the reduced voltage losses in NFA blend is under debate, reduced charge recombination rates and enhanced charge generation are two ingredients leading to the superior properties of NFA blends over fullerene devices.^[57] In the next section we will review NFA-based solar cells tackling the charge generation ability reported so far based on femtosecond-nanosecond transient absorption spectroscopy (TAS). In particular, with this technique, processes such as exciton decays and/or geminate recombination of bound polaron pairs can be studied, revealing for example variations in ΔE_{CT} at the donor/acceptor interface. Variations in the polymer singlet exciton lifetime with and without the acceptor material, allow the estimation of exciton recombination and dissociation. For example, **Figure 6a** shows the TA spectra of neat Pff4TBT-2DT: and Pff4TBT-2DT:FBR blend films, excited at 680 nm and probed at 1300

nm. The decay analysis showed that the exciton lifetime (τ) in the neat polymer ($\tau=237$ ps) is drastically reduced when the SM acceptor is added ($\tau=48$ ps), revealing that about 80% of excitons created on the polymer in the blend are dissociated and 20% are lost mainly due to coarse crystalline structure. The effective exciton dissociation plays the role for the concomitant high EQE and V_{oc} for both Pff4TBT-2DT:FBR and Pff4TBT-2DT:IDTBR blends.

Figure 6. Transient absorption spectra of neat PffBT4T-2DT and PffBT4T-2DT:FBR films excited at 680 nm and probed at 1300 nm a) and P3TEA:SFPDI blend (b), respectively. Reproduced with the permission from Refs.^[55,56]

Investigation of charge generation dynamics was also carried out on P3TEA:SFPDI blend system. The authors observed a fast photoinduced electron transfer from the donor to the acceptor, with the characteristic half-life decay of 3 ps, one order of magnitude faster than the singlet exciton lifetime of the donor (30 ps) (**Figure 6b**). Moreover, the authors found that about 23% of exciton population was already dissociated into charges within 100 fs and overall 87% of singlet excitons of the donor were dissociated in the blend, demonstrating an efficient and fast electron transfer, resulting in both high J_{sc} and V_{oc} .

Different from PCBM-based blends, NFA devices feature complementary absorption in the visible/near-infrared range. Therefore, different from fullerene system, in which, due to the relative low absorption of the acceptor molecule, mainly the electron transfer from the donor to

the acceptor were studied and only few examples reported the hole transfer mechanism from C60 to the donor, studying the hole transfer in NFA is utmost important to reveal the higher performance of this new class.

Li et al., investigated the hole transfer from ITIC to J71 despite the low energy difference between the HOMO levels of the two materials (0.11 eV), much smaller than the empirical threshold of 0.3 eV for effective exciton dissociation.^[51] To monitor the charge transfer mechanism the authors excite the blend system at 710 nm, where only ITIC absorbs. **Figure 7a-b** show the bleaching signal for both neat ITIC and J71:ITIC blend. However, for the neat acceptor, the signal is ascribed to the ground state bleach (GSB) (**Figure 7a**). Differently, in the blend film three different peaks are observed. In fact, in addition to the ITIC GSB, peaks at 540 nm and 590 nm appear, that correspond to the GSB signal of the donor polymer J71 (**Figure 7c**). **Figure 7c** shows compares the TA spectra for J71:ITIC blend at different delay. In agreement with an efficient hole transfer, the bleaching signals at 540 nm and 590 nm are built up with the decays of the signal at 710 nm. Moreover, **Figure 7d** compares the dynamics of neat ITIC and its blend with J71 probed at 710 nm. The data clearly indicates that upon addition of the donor polymer, the relaxation rates become faster and correspondingly, the buildup signal probed at 540 nm and 590 nm raised compared the neat polymer (**Figure 7e**), confirming that hole transfer from ITIC to J71 is the primary mechanisms in this blend system (**Figure 7f**).

Figure 7. Transient absorption signal recorded from the films of (a) neat ITIC and (b) J71: ITIC (1:1, w/w) blend excited by 710 nm. (c) Transient absorption spectra from the blend film excited

by 710nm (orange line) at different time delays. The lower panel shows the transient absorption spectra recorded at 1 ps from ITIC excited by 710 nm and J71 excited by 540nm (blue line), respectively. (d) Dynamics probed at 710 nm recorded from the films of neat ITIC and blend J71: ITIC (1:1w/w). (e) Dynamic curves probed at 540 and 590nm recorded from the film of blend. (f) A schematic diagram of the hole transfer in the film of J71: ITIC (1:1 w/w) blend. Reproduced with the permission from Ref.^[51]

Recently, Hou et al., reported a comprehensive study on the hole transfer mechanism for three different donor polymers depicting different HOMO level, blended with ITIC.^[64] The study aimed to reveal the role of the Δ HOMO between donor and acceptor materials as shown in **Figure 8a**. Similar to Li, TAS measurements are carried out on the three different blends by selectively exciting the NFA. **Figure 8b** shows the resulting polaron dynamic, that results from the hole transfer from ITIC to the donors. Interestingly, the early decay is almost the same in all samples, indicating that it is mostly dominated by exciton depletion dynamics, suggesting that donor:ITIC blends feature similar hole transfer kinetics, despite Δ HOMO values spanning from 0.04 eV to 0.35 eV. The authors suggested that for the NFA blends, the ultrafast charge transfer occurs due to the π -orbital overlapping between the donor and the acceptor which is also known as the formation of charge transfer state, and the driving force for the ultrafast charge transfer originates from the variation in the π -electron densities of the donor and the acceptor.

Figure 8. a) Energy level schematic of PBQ-0F, PBQ-QF, PBQ-4F, and ITIC and their relative Δ HOMO (or Δ LUMO) b) Time evolution of ITIC, PBQ-0F:ITIC, PBQ-QF:ITIC, and PBQ-4F:ITIC films monitored at 1.28 eV. Reproduced with the permission from Ref.^[64]

However, it is important to mention that the complete understanding of the ultrafast charge transfer mechanisms in these composites with a negligible Δ HOMO (or Δ LUMO) is still missing and several reports showed that NFA blends depicted higher exciton/geminate recombination rates compared to the fullerene counterparts.^[39,65] As reported by Durrant et al.,^[39] when the donor PffBT4T-OD is blended with either EH-IDTBR or PC₇₀BM, despite similar exciton separation dynamics (**Figure 9a**), EH-IDTBR based blends show a lower amplitude and shorter polaron lifetime compared to PC₇₀BM ones (**Figure 9b**). This increase in geminate recombination for the NFA system is probably due to the high LUMO level of the SM resulting in a lower energy driving force for charge separation. This increased geminate recombination is discussed in context with the reduced photocurrent generation in the NFA devices.

Figure 9. a) Transient absorption data of PffBT4T-2OD showing the time evolution of singlet exciton absorption probed at 1250 nm for the corresponding films (normalized at 1 ps) and b) showing the time evolution of singlet exciton (up to ≈ 100 ps) and polaron absorption (after ≈ 100 ps) for PffBT4T-2OD:PC₇₀BM and PffBT4T-2OD:EH-IDTBR blends probed at 1100 nm (normalized for photons absorbed). Reproduced with the permission from Ref.^[39]

2.2. Reduced Charge Carrier Recombination

In the previous chapter, we showed how low voltage losses together with the higher charge generation allow NFA blends with V_{oc} over 1.1 V and J_{sc} values approaching 20 mA cm^{-2} .^{[55][54]} We now turn our attention on charge carrier recombination processes that influence both charge transport and charge carrier lifetime in non-fullerene based solar cells. In general, organic solar devices deliver high fill factor (FF) when charge transport and recombination properties are matched simultaneously.^[41,66,67] Since the discovery of NFA, for both polymer and small molecule, only one example of devices with high FF values over 75% is reported.^[68,69] This is in strictly contrast with fullerene-based devices.^[66] One of the reason of the low FF is the lower charge carrier mobility (μ) of SMA compared to PCBM derivate.^[1] In fact, fullerene based systems delivering high FF values are often reporting μ in the order of 10^{-4}

$3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$,^[70] whereas, NFA blends show at least μ of one order of magnitude lower.^[3] Organic semiconductors are in general known to be materials with lower mobility compared to the inorganic counterparts. As such, the bimolecular recombination rate of holes and electrons, usually referred to as Langevin recombination, is typically an important loss mechanism.^[71] The Langevin recombination coefficient β_L is given by equation (4):

$$\beta_L = \frac{q^*(\mu_h + \mu_e)}{\varepsilon_0 \varepsilon} \quad (4)$$

where μ_h and μ_e are the effective charge carrier mobility of holes and electrons, respectively, ε_0 is the vacuum and ε the relative permittivity. Notably, if the recombination of electrons and holes is not instant as they meet and an electron hole pair has a significant chance to split again, after their encounter, the Langevin model will not be able to describe the recombination dynamics correctly.^[71] This is typically described as reduced Langevin recombination. Comparing the measured bimolecular recombination factor (β) with the calculated Langevin prefactor informs about the recombination mechanism, where $\beta/\beta_L < 1$ indicates reduced Langevin recombination.

Recently, we reported a NFA system based on P3HT:O-IDTBR showing an unprecedentedly low recombination rate.^[57] Time of flight (TOF) measurements were carried out to obtain the charge carrier mobility of the blend, thus calculating β_L of $2.2 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$. The bimolecular recombination coefficient, instead, was obtained by time delay-dependent photoinduced charge carrier extraction by linearly increasing voltage (Photo-CELIV) measurements.^[72] **Figure 10a** reveals that β is time independent, which informs that P3HT:O-IDTBR features pure 2nd order recombination. Moreover, the calculated average value of β amounts to $4.2 \times 10^{-14} \text{ cm}^3\text{s}^{-1}$. The resulting ratio β/β_L of 1.9×10^{-4} indicates that the P3HT: O-IDTBR blend exhibits unprecedented strong non-Langevin type behavior with an extremely low recombination coefficient. Interestingly, bimolecular recombination factors in the order of $\sim 2 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ have been observed before for fullerene-based system,^[73] but recombination factors as low as 1.9×10^{-14}

cm³s⁻¹ are exceptional. Moreover, considering the extremely low recombination constant, thick active layer devices were fabricated, utmost important for technological applications.^[74] This rare case of thickness independent power conversion efficiencies is depicted in **Figure 10b** for a thickness regime from 80-450. This is impressive considering that most high-performance polymer blends show significant losses in power conversion efficiency for active layer thicknesses beyond ~200 nm, mostly due to charge transport limited recombination.^[75] While we already showed that P3HT:IDTBR exhibits non-Langevin recombination behavior, the calculation of the carrier lifetime is crucial to further elucidate the photovoltaic performance of IDTBR-based devices.^{[76][77]} Transient photovoltage (TPV) measurements under open circuit condition, gave access to the perturbation charge carrier lifetime ($\tau_{\Delta n}$). P3HT:IDTBR devices depicted enhanced carrier lifetime ($\tau=8.61 \mu\text{s}$) under 1 sun illumination compared to P3HT:PCBM ($\tau=2.85 \mu\text{s}$) and other high performance fullerene-based devices ($\tau=2.31 \mu\text{s}$). Additionally, combined TPV / charge extraction (CE) measurements – the latter to obtain the average charge carrier density (n) - allowed insight into the exact recombination order (R).^{[41][76]} **Figure 10c** shows $\tau_{\Delta n}$ vs n under V_{oc} condition at different light intensity levels. Analysis of the data according to a power law dependence of the form $\tau_{\Delta n} = \tau_{\Delta n0} \left(\frac{n_0}{n}\right)^\lambda$, where $\tau_{\Delta n0}$ and n_0 are constants and λ is the so-called recombination exponent, reveals P3HT:IDTBR devices with a reduced λ of ~1.1 and consequentially a recombination order $R = \lambda + 1$ equal to 2.1, confirming the absence of parasitic recombination, such as trap-assisted recombination as well as morphological defects in P3HT:IDTBR based organic solar cells.

Figure 10. a) Charge carrier density and bimolecular recombination coefficient as a function of $t_d + t_{\text{max}}$ calculated from photo-CELIV measurements for P3HT:O-IDTBR solar cells. b) Power conversion efficiency as a function of the blend active layer thickness for P3HT:O-IDTBR based devices. c) Charge carrier lifetime τ as a function of charge density n under V_{oc} condition (from 0.2 to 4 suns). Reproduced with the permission from Ref.^[57]

Charge transport investigation were also carried out on Pff4TBT-2DT:FBR devices in comparison to Pff4TBT-2DT:PC₇₀BM solar cells. Calculated higher charge carrier mobility in the NFA system (**Figure 11a**) compared to PCBM blends was reported. Moreover, the bimolecular recombination coefficient and β/β_L were calculated for both NFA and fullerene systems. with $\sim 10^{-2}$ for Pff4TBT-2DT:FBR and 10^{-1} for Pff4TBT-2DT:PC₇₀BM blends, confirming the suppressed bimolecular recombination between free charge carriers, which further contributes to an enhanced V_{oc} in the NFA systems.

Figure 11. a) Effective device mobility as a function of charge carrier density, measured by charge extraction at short circuit for PffBT4T-2DT:PCBM (green) and PffBT4T-2DT:FBR (blue). b) Langevin recombination rate constant (circles) and the measured bimolecular

recombination rate (open squares) measured from transient photovoltage (TPV) and charge extraction (CE) measurements at open circuit. Reproduced with the permission from Ref.^[55]

Charge carrier recombination processes are intimately related to the microstructure of the active layer.^[78] Different from fullerene-based devices, in which PCBM aggregates enhance charge separation due to long range electron transfer reaction via crystalline interfaces,^[79] NFA materials tend to form characteristics large crystalline domains and in contrast to fullerenes, when blended with the donor materials, the crystallinity of both donor and acceptor are not significantly perturbed.^{[40][1]} This was first observed by Holliday et al for P3HT:O-IDTBR and P3HT:EH-IDTBR.^[1] The design principles for IDTBR based acceptors were further increased by putting emphasis on the planarity of the backbone in order to induce crystallization and the formation of pure acceptor domains. As a result, extremely low charge recombination rates were obtained for this system.^[57]

One step further in the design of NFA composites was reported by Baran et al on ternary P3HT:IDTBR composites,^[40] The addition of a second acceptor (IDFBR), leading to the so-called ternary configuration with two acceptors, was introduced to enhance light harvesting. However, not only J_{sc} was improved in the ternary system but also V_{oc} and FF were enhanced: first, due to an increased electronic bandgap for the ternary blend and second, due to an increased charge carrier lifetime as depicted in **Figure 12**.

Figure 12. a) V_{oc} and charge carrier lifetime versus average excess charge density. b) Correlation between photon energies (at $\text{EQE}=10^{-2}$) and V_{oc} of P3HT:IDTBR:IDFBR devices as a function of IDFBR content. c) TPV data for corresponding P3HT:IDTBR and P3HT:IDTBR:IDFBR blends at V_{oc} in response to a small additional light pulse. Reproduced with the permission from Ref.^[40]

3. Superior device stability of small molecule acceptor based solar cells

Although great progress has been achieved in NFA devices and PCE of over 13% were reported,^[21] both, scalability of the materials and device stability need to be addressed for becoming competitive with other thin film technologies. In this context, blends of P3HT:IDTBR do feature the criteria required above, leading to improved shelf-life and photo-oxidation stability, together with an easy scalability of P3HT. **Figure 13** shows the temporal evolution of all photovoltaic parameters under accelerated lifetime testing of P3HT:O-IDTBR

devices operated at open circuit in regulated environment ($O_2 < 1\text{ppm}$, $H_2O < 1\text{ppm}$) under solar simulator light.^[38] Notably, in the case of aged non-fullerene based devices V_{oc} remains unaffected and J_{sc} slightly increases ($\sim 4\%$) when compared with time zero, while only FF shows a significant drop of $\sim 10\%$. Overall, light-soaked P3HT:O-IDTBR solar cells lose about 5% of power conversion efficiency in the course of 2000 h of light exposure. Importantly, the PCE evolution of P3HT:O-IDTBR based devices is burn-in free, i.e., it does not show the typical exponential performance loss and reflects one of the most stable long-term behaviors observed to date for solution-processed solar cells under accelerated lifetime testing condition.

Figure 13. Normalized parameters of J_{sc} , V_{oc} , FF and PCE of P3HT:O-IDTBR and P3HT:PCBM solar cells in the course of 2000 h of light exposure. The traces for P3HT:O-IDTBR correspond to average values of 22 individual devices of different P3HT batches. The P3HT:PCBM data is an average of 6 devices. Reproduced with the permission from Ref.^[57]

Moreover, extrapolating the lifetime energy yield (LEY) according to Roesch et al.,^[80] P3HT:O-IDTBR depicted a maximum energy yield that is a factor of three larger compared to P3HT:PCBM blends. Furthermore, the FF loss observed in the NFA based devices after photo-aging was attributed to increased trap state, most likely originated from interface defects that induce a deviation from an ideal 2nd order recombination.

The improved photofastness of P3HT:O-IDTBR blend was firstly reported by Holliday and co-workers,^[1] in comparison with state-of-the-art polymer:fullerene blends, such as PTB7 or PTB7-th based devices. **Figure 14a** shows the evolution of the PCE over time for NFA vs PCBM based systems under ambient condition in the dark, showing the superior oxidative and morphological stability of O-IDTBR blends (**Figure 14a**).

Figure 14. a) Oxidative stability of O-IDTBR:P3HT device efficiencies (PCE) compared with other high-performance polymer:fullerene systems. Devices were stored in the dark under ambient conditions between measurements. b) Shelf storage lifetime (dark, in air) comparison

of P3HT:IDTBR:IDFBR device efficiencies with other polymer:fullerene systems. Devices were exposed to ambient conditions over a 1,200 h duration or until the loss of any diode behaviour. c) Photo-stability of P3HT:IDTBR:IDFBR device and polymer:fullerene solar cells (in air, un-encapsulated, under AM1.5 illumination at 1 sun) for 90h. Reproduced with the permission from Refs.^{[1][40]}

Later, Baran et al.,^[40] with the incorporation of IDFBR in P3HT:O-IDTBR binary system, showed improved shelf-life stability for the ternary system for more than 1000 h in air (**Figure 14b**). In addition the authors also proved the photostability of binary and ternary devices under light illumination in air. As shown in **Figure 14c**, ternary blends retained 85% of its initial performance after 90h, while high-efficiency systems, such as PTB7-Th:PC₇₀BM show PCE of more than 80% for the same exposure time.

Figure 15. a) Normalized PCEs of the devices after long-term light soaking without UV light maintained below 50 °C thermal stress and b) annealing at 85 °C, under nitrogen. Reproduced with the permission from Ref.^[39]

Interestingly, Durrant and co-workers,^[39] reported the similar burn-in free trend of P3HT:O-IDTBR devices, for a high efficient NFA based on PffBT4T-2OD:EH-IDTBR. As reported in **Figure 15a**, NFA blends showed no light induced efficiency loss for 60h exposure, whereas the polymer:PC70BM blends depicted the characteristics burn-in loss. The same devices were also tested under 85°C thermal stress in the dark (**Figure 15b**). Again, PffBT4T-2OD:EH-IDTBR showed substantially improved stability compared to PffBT4T-2OD:PC₇₀BM devices.

4. Conclusion and Outlook

Fullerene-free organic solar cells and in particular small molecule NFA blends are facing a bright future in the field on thin film technology. Major limitations of fullerene-based OPV such as long-term stability, E_g to open circuit voltage loss and photocurrent generation are largely mitigated with the replacement of C60 and C70 derivatives with NFA. Currently, (A)-A-D-A-(A) type acceptors (IDTBR and ITIC) are the most used in high-efficient blends due to their strong electron-withdrawing units and planar and rigid configuration for efficient molecular packing. In particular, NFA-based devices frequently win over their pendant fullerene based devices due to relatively pure, crystalline phases and sharp polymer/acceptor interphases, which tackle the three milestones of any photovoltaic technology: stability, efficiency and materials availability. In fact, the absence of burn-in removes the need for a *stabilized lifetime* and allows indexing the predicted lifetime to the time zero performance; efficiencies up to 15% are expected to be reported within the next couple of years. In addition to efficiency, NFAs and especially P3HT:NFA blends impress with the highest cost efficiency of any polymer:fullerene blends according to energy return on investment (EROI) as recently reported. Considering the high individually reported values of J_{sc} (22 mA cm⁻²) and V_{oc} (1.2 V) of NFAs and comparing these values with perovskite devices, is clear that the gap between these

technologies is decreasing. The challenges will be to simultaneously achieve these values, together with high FF in one device. Therefore, research efforts have to be directed to:

- i) Reveal the origin of the non-radiative voltage loss, that limits the EQE_{EL} of non-fullerene devices;
- ii) Extend the absorption window of NFA blends beyond 800-850 nm to achieve high photocurrent, while maintaining high voltage.
- iii) Understand the causes of the slow recombination rates and in particular reveal whether NFA solar cells are dominated by a diffusion-controlled rather than drift-controlled model;

We expect, in parallel with the abovementioned challenges, novel non-fullerene acceptor material design, interfaces and device engineering toward pushing the limit for organic solar cells.

References

- [1] S. Holliday, R. S. Ashraf, A. Wadsworth, D. Baran, S. A. Yousaf, C. B. Nielsen, C.-H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C. J. Brabec, A. Salleo, J. R. Durrant, I. McCulloch, *Nat. Commun.* **2016**, 7, 11585.
- [2] C. B. Nielsen, S. Holliday, H.-Y. Chen, S. J. Cryer, I. McCulloch, *Acc. Chem. Res.* **2015**, 48, 2803.
- [3] W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, F. Gao, J. Hou, *Adv. Mater.* **2016**, 28, 4734.
- [4] S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant, J. Nelson, I. McCulloch, *J. Am. Chem. Soc.* **2015**, 137, 898.
- [5] D. Mori, H. Benten, I. Okada, H. Ohkita, S. Ito, *Adv. Energy Mater.* **2014**, 4, 1301006.
- [6] N. Zhou, H. Lin, S. J. Lou, X. Yu, P. Guo, E. F. Manley, S. Loser, P. Hartnett, H. Huang, M. R. Wasielewski, L. X. Chen, R. P. H. Chang, A. Facchetti, T. J. Marks, *Adv. Energy Mater.* **2014**, 4, 1300785.
- [7] C. Mu, P. Liu, W. Ma, K. Jiang, J. Zhao, K. Zhang, Z. Chen, Z. Wei, Y. Yi, J. Wang, S. Yang, F. Huang, A. Facchetti, H. Ade, H. Yan, *Adv. Mater.* **2014**, 26, 7224.
- [8] P. E. Hartnett, A. Timalina, H. S. S. R. Matte, N. Zhou, X. Guo, W. Zhao, A. Facchetti, R. P. H. Chang, M. C. Hersam, M. R. Wasielewski, T. J. Marks, *J. Am. Chem. Soc.* **2014**, 136, 16345.
- [9] Y. Zang, C.-Z. Li, C.-C. Chueh, S. T. Williams, W. Jiang, Z.-H. Wang, J.-S. Yu, A. K.-Y. Jen, *Adv. Mater.* **2014**, 26, 5708.
- [10] Y.-J. Hwang, T. Earmme, B. a. E. Courtright, F. N. Eberle, S. a. Jenekhe, *J. Am. Chem. Soc.* **2015**, 137, 4424.
- [11] Y.-J. Hwang, B. a. E. Courtright, A. S. Ferreira, S. H. Tolbert, S. a. Jenekhe, *Adv. Mater.* **2015**, 27, 4578.

- [12] Z. Tang, B. Liu, A. Melianas, J. Bergqvist, W. Tress, Q. Bao, D. Qian, O. Inganäs, F. Zhang, *Adv. Mater.* **2015**, 27, 1900.
- [13] J. Zhao, Y. Li, H. Lin, Y. Liu, K. Jiang, C. Mu, T. Ma, J. Y. Lin Lai, H. Hu, D. Yu, H. Yan, *Energy Environ. Sci.* **2015**, 8, 520.
- [14] O. K. Kwon, J.-H. Park, D. W. Kim, S. K. Park, S. Y. Park, *Adv. Mater.* **2015**, 27, 1951.
- [15] S. M. McAfee, J. M. Topple, I. G. Hill, G. C. Welch, *J. Mater. Chem. A* **2015**, 3, 16393.
- [16] Y. Lin, F. Zhao, Y. Wu, K. Chen, Y. Xia, G. Li, S. K. K. Prasad, J. Zhu, L. Huo, H. Bin, Z. Zhang, X. Guo, M. Zhang, Y. Sun, F. Gao, Z. Wei, W. Ma, C. Wang, J. Hodgkiss, Z. Bo, O. Inganäs, Y. Li, X. Zhan, *Adv. Mater.* **2016**, 1.
- [17] Y. Lin, F. Zhao, Q. He, L. Huo, Y. Wu, T. C. Parker, W. Ma, Y. Sun, C. Wang, D. Zhu, A. J. Heeger, S. R. Marder, X. Zhan, *J. Am. Chem. Soc.* **2016**, 138, 4955.
- [18] L. Gao, Z.-G. Zhang, L. Xue, J. Min, J. Zhang, Z. Wei, Y. Li, *Adv. Mater.* **2016**, 28, 1884.
- [19] H. Yao, Y. Chen, Y. Qin, R. Yu, Y. Cui, B. Yang, S. Li, K. Zhang, J. Hou, *Adv. Mater.* **2016**, 28, 8283.
- [20] S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, J. Hou, *Adv. Mater.* **2016**, 28, 9423.
- [21] W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, *J. Am. Chem. Soc.* **2017**, 139, 7148.
- [22] H. Kang, G. Kim, J. Kim, S. Kwon, H. Kim, K. Lee, *Adv. Mater.* **2016**, 28, 7821.
- [23] R. Po, A. Bernardi, A. Calabrese, C. Carbonera, G. Corso, A. Pellegrino, *Energy Environ. Sci.* **2014**, 7, 925.
- [24] G. Li, R. Zhu, Y. Yang, *Nat. Photonics* **2012**, 6, 153.
- [25] A. A. Bakulin, J. C. Hummelen, M. S. Pshenichnikov, P. H. M. Van Loosdrecht, *Adv.*

- Funct. Mater.* **2010**, 20, 1653.
- [26] C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia, S. P. Williams, *Adv. Mater.* **2010**, 22, 3839.
- [27] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *Appl. Phys. Lett.* **2001**, 78, 841.
- [28] T. Heumueller, T. M. Burke, W. R. Mateker, I. T. Sachs-Quintana, K. Vandewal, C. J. Brabec, M. D. McGehee, *Adv. Energy Mater.* **2015**, 5, 1500111.
- [29] C. Zhang, A. Mumyatov, S. Langner, J. D. Perea, T. Kassar, J. Min, L. Ke, H. Chen, K. L. Gerasimov, D. V. Anokhin, D. A. Ivanov, T. Ameri, A. Osvet, D. K. Susarova, T. Unruh, N. Li, P. Troshin, C. J. Brabec, *Adv. Energy Mater.* **2016**, 1601204.
- [30] N. Li, J. D. Perea, T. Kassar, M. Richter, T. Heumueller, G. J. Matt, Y. Hou, N. S. Güldal, H. Chen, S. Chen, S. Langner, M. Berlinghof, T. Unruh, C. J. Brabec, *Nat. Commun.* **2017**, 8, 14541.
- [31] J. D. Perea, S. Langner, M. Salvador, B. Sanchez-Lengeling, N. Li, C. Zhang, G. Jarvas, J. Kontos, A. Dallos, A. Aspuru-Guzik, C. J. Brabec, *J. Phys. Chem. C* **2017**, 121, 18153.
- [32] W. R. Mateker, M. D. McGehee, *Adv. Mater.* **2017**, 29, 1603940.
- [33] M. Salvador, N. Gasparini, J. D. Perea, S. H. Paleti, A. Distler, L. N. Inasaridze, P. A. Troshin, L. Lüer, H.-J. Egelhaaf, C. Brabec, *Energy Environ. Sci.* **2017**.
- [34] T. Heumueller, W. R. Mateker, I. T. Sachs-Quintana, K. Vandewal, J. a. Bartelt, T. M. Burke, T. Ameri, C. J. Brabec, M. D. McGehee, *Energy Environ. Sci.* **2014**, 7, 2974.
- [35] M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* **2012**, 24, 580.
- [36] T. Heumueller, W. R. Mateker, A. Distler, U. F. Fritze, R. Cheacharoen, W. H. Nguyen, M. Biele, M. Salvador, M. von Delius, H.-J. Egelhaaf, M. D. McGehee, C. J. Brabec, *Energy Environ. Sci.* **2015**, 9, 247.

- [37] J. Adams, G. D. Spyropoulos, M. Salvador, N. Li, S. Strohm, L. Lucera, S. Langner, F. Machui, H. Zhang, T. Ameri, M. M. Voigt, F. C. Krebs, C. J. Brabec, *Energy Environ. Sci.* **2015**, 8, 169.
- [38] N. Gasparini, M. Salvador, S. Strohm, T. Heumueller, I. Levchuk, A. Wadsworth, J. H. Bannock, J. C. de Mello, H.-J. Egelhaaf, D. Baran, I. McCulloch, C. J. Brabec, *Adv. Energy Mater.* **2017**, 7, 1700770.
- [39] H. Cha, J. Wu, A. Wadsworth, J. Nagitta, S. Limbu, S. Pont, Z. Li, J. Searle, M. F. Wyatt, D. Baran, J.-S. Kim, I. McCulloch, J. R. Durrant, *Adv. Mater.* **2017**, 1701156, 1701156.
- [40] D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Röhr, S. Holliday, A. Wadsworth, S. Lockett, M. Neophytou, C. J. M. Emmott, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant, I. McCulloch, *Nat. Mater.* **2016**, 16, 363.
- [41] N. Gasparini, X. Jiao, T. Heumueller, D. Baran, G. J. Matt, S. Fladischer, E. Spiecker, H. Ade, C. J. Brabec, T. Ameri, *Nat. Energy* **2016**, 1, 16118.
- [42] T. Ameri, P. Khoram, J. Min, C. J. Brabec, *Adv. Mater.* **2013**, 25, 4245.
- [43] Y. Cui, H. Yao, B. Gao, Y. Qin, S. Zhang, B. Yang, C. He, B. Xu, J. Hou, *J. Am. Chem. Soc.* **2017**, 139, 7302.
- [44] T. Ameri, N. Li, C. J. Brabec, *Energy Environ. Sci.* **2013**, 6, 2390.
- [45] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, J. V Manca, *Nat. Mater.* **2009**, 8, 904.
- [46] S. a. Hawks, F. Deledalle, J. Yao, D. G. Rebois, G. Li, J. Nelson, Y. Yang, T. Kirchartz, J. R. Durrant, *Adv. Energy Mater.* **2013**, 3, 1201.
- [47] K. Vandewal, S. Albrecht, E. T. Hoke, K. R. Graham, J. Widmer, J. D. Douglas, M. Schubert, W. R. Mateker, J. T. Bloking, G. F. Burkhard, A. Sellinger, J. M. J. Fréchet, A. Amassian, M. K. Riede, M. D. McGehee, D. Neher, A. Salleo, *Nat. Mater.* **2014**, 13,

- [48] T. Kirchartz, U. Rau, *Phys. Status Solidi* **2008**, 205, 2737.
- [49] S. M. Menke, A. Sadhanala, M. Nikolka, N. A. Ran, M. K. Ravva, S. Abdel-Azeim, H. L. Stern, M. Wang, H. Sirringhaus, T.-Q. Nguyen, J.-L. Brédas, G. C. Bazan, R. H. Friend, *ACS Nano* **2016**, 10, 10736.
- [50] K. Vandewal, A. Gadisa, W. D. Oosterbaan, S. Bertho, F. Banishoeib, I. Van Severen, L. Lutsen, T. J. Cleij, D. Vanderzande, J. V. Manca, *Adv. Funct. Mater.* **2008**, 18, 2064.
- [51] H. Bin, L. Gao, Z.-G. Zhang, Y. Yang, Y. Zhang, C. Zhang, S. Chen, L. Xue, C. Yang, M. Xiao, Y. Li, *Nat. Commun.* **2016**, 7, 13651.
- [52] H. Yao, R. Yu, T. J. Shin, H. Zhang, S. Zhang, B. Jang, M. A. Uddin, H. Y. Woo, J. Hou, *Adv. Energy Mater.* **2016**.
- [53] F. Liu, Z. Zhou, C. Zhang, J. Zhang, Q. Hu, T. Vergote, F. Liu, T. P. Russell, X. Zhu, *Adv. Mater.* **2017**, 29.
- [54] H. Yao, Y. Cui, R. Yu, B. Gao, H. Zhang, J. Hou, *Angew. Chemie Int. Ed.* **2017**, 56, 3045.
- [55] D. Baran, T. Kirchartz, S. Wheeler, S. Dimitrov, M. Abdelsamie, J. Gorman, R. S. Ashraf, S. Holliday, A. Wadsworth, N. Gasparini, P. Kaienburg, H. Yan, A. Amassian, C. J. Brabec, J. R. Durrant, I. McCulloch, *Energy Environ. Sci.* **2016**, 9, 3783.
- [56] J. Liu, S. Chen, D. Qian, B. Gautam, G. Yang, J. Zhao, J. Bergqvist, F. Zhang, W. Ma, H. Ade, O. Inganäs, K. Gundogdu, F. Gao, H. Yan, *Nat. Energy* **2016**, 1, 16089.
- [57] N. Gasparini, M. Salvador, T. Heumueller, M. Richter, A. Classen, S. Shrestha, G. J. Matt, S. Holliday, S. Strohm, H.-J. Egelhaaf, A. Wadsworth, D. Baran, I. McCulloch, C. J. Brabec, *Adv. Energy Mater.* **2017**, 1701561, 1701561.
- [58] B. Xiao, A. Tang, J. Yang, Z. Wei, E. Zhou, *ACS Macro Lett.* **2017**, 6, 410.
- [59] J. Yao, T. Kirchartz, M. S. Vezie, M. A. Faist, W. Gong, Z. He, H. Wu, J. Troughton,

- T. Watson, D. Bryant, J. Nelson, *Phys. Rev. Appl.* **2015**, 4, 14020.
- [60] K. Vandewal, Z. Ma, J. Bergqvist, Z. Tang, E. Wang, P. Henriksson, K. Tvingstedt, M. R. Andersson, F. Zhang, O. Inganäs, *Adv. Funct. Mater.* **2012**, 22, 3480.
- [61] J. Benduhn, K. Tvingstedt, F. Piersimoni, S. Ullbrich, Y. Fan, M. Tropiano, K. A. McGarry, O. Zeika, M. K. Riede, C. J. Douglas, S. Barlow, S. R. Marder, D. Neher, D. Spoltore, K. Vandewal, *Nat. Energy* **2017**, 2, 17053.
- [62] H. J. Queisser, *Mater. Sci. Eng. B* **2009**, 159–160, 322.
- [63] A. A. Bakulin, A. Rao, V. G. Pavelyev, P. H. M. van Loosdrecht, M. S. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne, R. H. Friend, *Science (80-.)*. **2012**, 335, 1340.
- [64] Z. Zheng, O. M. Awartani, B. Gautam, D. Liu, Y. Qin, W. Li, A. Bataller, K. Gundogdu, H. Ade, J. Hou, *Adv. Mater.* **2016**, 3.
- [65] F. Yang, D. Qian, A. H. Balawi, Y. Wu, W. Ma, F. Laquai, Z. Tang, F. Zhang, W. Li, *Phys. Chem. Chem. Phys.* **2017**, 19, 23990.
- [66] D. Bartsaghi, I. D. C. Pérez, J. Kniepert, S. Roland, M. Turbiez, D. Neher, L. J. A. Koster, *Nat. Commun.* **2015**, 6, 7083.
- [67] X. Guo, N. Zhou, S. J. Lou, J. Smith, D. B. Tice, J. W. Hennek, R. P. Ortiz, J. T. L. Navarrete, S. Li, J. Strzalka, L. X. Chen, R. P. H. Chang, A. Facchetti, T. J. Marks, *Nat. Photonics* **2013**, 7, 825.
- [68] B. Guo, W. Li, X. Guo, X. Meng, W. Ma, M. Zhang, Y. Li, *Adv. Mater.* **2017**, 1702291, 1.
- [69] B. Qiu, L. Xue, Y. Yang, H. Bin, Y. Zhang, C. Zhang, M. Xiao, K. Park, W. Morrison, Z. G. Zhang, Y. Li, *Chem. Mater.* **2017**, 29, 7543.
- [70] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Commun.* **2014**, 5, 5293.
- [71] L. J. a. Koster, V. D. Mihailetschi, P. W. M. Blom, *Appl. Phys. Lett.* **2006**, 88, 52104.
- [72] M. Stephen, K. Genevičius, G. Juška, K. Arlauskas, R. C. Hiorns, *Polym. Int.* **2017**, 66,

- 13.
- [73] T. M. Clarke, J. Peet, P. Denk, G. Dennler, C. Lungenschmied, A. J. Mozer, *Energy Environ. Sci.* **2012**, 5, 5241.
- [74] N. Gasparini, L. Lucera, M. Salvador, M. Prosa, G. D. Spyropoulos, P. Kubis, H.-J. Egelhaaf, C. J. Brabec, T. Ameri, *Energy Environ. Sci.* **2017**, 10, 885.
- [75] Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.* **2010**, 22, 135.
- [76] C. G. Shuttle, B. O'Regan, a. M. Ballantyne, J. Nelson, D. D. C. Bradley, J. De Mello, J. R. Durrant, *Appl. Phys. Lett.* **2008**, 92, 90.
- [77] C. G. Shuttle, N. D. Treat, J. D. Douglas, J. M. J. Fréchet, M. L. Chabinyc, *Adv. Energy Mater.* **2012**, 2, 111.
- [78] X. Jiao, L. Ye, H. Ade, *Adv. Energy Mater.* **2017**, 1700084, 1700084.
- [79] A. C. Jakowetz, M. L. Böhm, J. Zhang, A. Sadhanala, S. Huettnner, A. A. Bakulin, A. Rao, R. H. Friend, *J. Am. Chem. Soc.* **2016**, 138, 11672.
- [80] R. Roesch, T. Faber, E. von Hauff, T. M. Brown, M. Lira-Cantu, H. Hoppe, *Adv. Energy Mater.* **2015**, 5, 1501407.
- [81] Z. Fei, F. Eisner, X. Jiao, M. Azzouzi, J. Roehr, Y. Han, M. Shahid, A. Chesman, C. Easton, C. McNeill, T. Anthopoulos, J. Nelson, M. Heeney, *Adv. Mat.*, **2017**, accepted.

In this contribution, we review the current understanding of the relevant photo-physical processes as well as the superior light and thermal stability of efficient non-fullerene acceptor (NFA) small molecules in comparison to fullerenes based composites.