Organic solar cells based on anthracene-containing PPE-PPVs and non-fullerene acceptors

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Abstract

Lately, non-fullerene acceptors (NFAs) have received increasing attention for use in polymer-based bulk-heterojunction (BHJ) organic solar cells (OSCs), as improved photovoltaic performance compared to classical polymer-fullerene blends could be demonstrated. In this study, polymer solar cells based on a statistically substituted anthracene-containing poly(*p*-phenyleneethynylene)-*alt*-poly(*p*-phenylenevinylene)s (PPE-PPVs) copolymer (**AnE-PVstat**) as donor in combination with a number of different electron accepting materials were investigated. Strong photoluminescence quenching of the polymer donor indicates intimate intermixing of both materials. However, the photovoltaic performances were found to be poor compared to blends that use fullerene as acceptor. Time-delayed collection field (TDCF) measurements demonstrate: charge generation is field-independent, but bimolecular recombination processes limit the fill factor and thus the efficiency of devices.

Keywords

Non-fullerene acceptors (NFA), Bulk-heterojunction (BHJ), Organic solar cell (OSC)

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Introduction

The increase in the global population is continually putting more and more strain on energy supply, leading to excessive exploitation of conventional energy resources such as fossil fuels. Low cost and abundant energy solutions can release this strain to some extent (Holdren 1991; IEA 2015). Hence, the search for low-cost renewable energy solutions is currently considered top priority in energy research. The deployment of organic photovoltaics (OPV) as a renewable energy technology has shown promise of reducing both, direct technology costs and environmental impact. This technology offers greater ease of fabrication, less energy-intensive production and the possibility roll-to-roll manufacturing (Günes et al. 2007; Krebs et al. 2010; Mulligan et al. 2014; Zhao et al. 2017). In the last decade research on OPVs have seen a steady and fast growth with improved efficiencies now above 13%, obtained with bulk heterojunction OSCs (Zhao et al. 2017). One of its most prominent attractions is the ability to be processed from solution and the applicability of fast mass printing techniques that allow for high production output with relatively low material consumption (Cao and Xue 2014). Fullerene derivatives are one of the most fundamental components in commercially available polymer solar cells. They are used as an acceptor, typically blended with an electron-rich donor to yield the photoactive layer of the solar cells (Hummelen et al. 1995; Wienk et al. 2003). Although, there are quite a number of advantages of applying fullerenes in polymer solar cells, including an energetically low-lying lowest unoccupied molecular orbital (LUMO) (Allemand et al. 1991), ultra-fast charge transfer, and high electron mobility (Singh et al. 2005; Thompson and Fréchet 2008), their commercial application is limited. A high synthesis cost is one of the most critical hurdles preventing the application of fullerene derivatives. Scientifically, impurities created during synthesis, weak absorption in the solar spectral range limiting photon harvesting to the absorption of the donor material (Ren et al. 2011), and chemical and energetic tenability are major issues. Non-fullerene acceptors (NFAs) have recently emerged as replacement of fullerenes, and over the past few years have received the increased attention of a growing research community. Organic based molecular NFAs have developed as excellent materials for use in high-performance bulk heterojunction solar cells (Eftaiha et al. 2014; McAfee et al. 2015; Sonar et al. 2011), some of the best and most studied NFAs are based upon the perylene diimide chromophore (Kozma and Catellani 2013; Liu et al. 2016), and have demonstrated photovoltaic power conversion efficiencies (PCE) as high as 9.5% (Liang et al. 2017).

The acceptors used in this study are molecular-based materials with an A-D-A structural motif, where A is an acceptor moiety and D a donor moiety. This molecular structure allows for a considerable flexibility in molecular design, bandgap engineering, and fine-tuning the absorption spectrum, and blend morphology (Liang et al. 2017; Nielsen et al. 2015). Furthermore, it allows for a broad range of synthetic approaches. Also through the modification of the attached side chains, their solubility in different solvents, as well as the blend morphology, can be tuned. Hence it becomes readily possible to refrain from halogenated solvents (Wadsworth et al. 2017) without losing performance (Dayneko et al. 2017), which was already shown for some polymer:NFA's blends. All these facts promise a bright future for NFA based OSCs (Bicciocchi et al. 2015).

In this work, we present a polymer donor, a PPE-PPV derivative called **AnE-PVstat**, in combination with NFAs that show a complementary absorption spectrum. All blends showed strong quenching of photoluminescence but unfortunately no or only a deficient photovoltaic performance. The reasons behind the poor photovoltaic performance will be elucidated in the following.

Experimental

Materials

Polymer:NFA blend solutions were prepared from 2:3 (mass% ratio) mixtures. The synthesis of **AnE-PVstat** is described elsewhere (Egbe et al. 2010; Kivrak et al. 2017a; Kivrak et al. 2017b). In order to compare with a standard acceptor material, **PCBM** (Solenne) was used as received. The chemical structure of **AnE-PVstat**, **PCBM** and NFAs are shown in **Figure 1**. The synthesis of **ITIC** and PDI based non-fullerene acceptors were described elsewhere (Cann et al. 2017a; Cann et al. 2017b; Lin et al. 2015; McAfee et al. 2017).

Figure 1: Molecular structure of **AnE-PVstat** (C_8H_{17} = *n*-octyl or 2-ethylhexyl), **PCBM**, **ITIC** (C_6H_{13} = *n*-hexyl), **PDI₂Ac₂ (Pa2)** (C_6H_{13} = *n*-hexyl), **DPP-(Ac-PDI)₂ (DaP2)** (C_6H_{13} = *n*-hexyl, C_8H_{17} = 2-ethylhexyl) and **TII-(Ac-PDI)₂ (TaP2)** (C_6H_{13} = *n*-hexyl, C_8H_{17} = 2-ethylhexyl).

The donor material is a side chain based statistical copolymer with a random distribution of segments of linear octyloxy side chains and of branched 2-ethylhexyloxy side chains on an anthracene-containing poly(*p*-phenylene-ethynylene)-*alt*-poly(*p*-phenylene-vinylene) (PPE-PPV) backbone known as **AnE-PVstat** polymer. The synthesis of this polymer was described in detail in (Egbe et al. 2010), the fullerene acceptor used is a derivative of C₆₀ known as **PCBM**. The NFA, **ITIC** is based on the bulky seven-ring fused core (indacenodithieno [3,2-*b*]thiophene, IT), end-capped with 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile (INCN) groups, and with four 4-hexylphenyl groups substituted on it. From the original publication on the synthesis of **ITIC**, it is reported to have strong and broad absorption, low-lying LUMO and highest occupied molecular orbital (HOMO) energy levels, good electron transport ability, and good miscibility with polymer donors, the synthesis of this material is detailed previously (Lin et al. 2015). Three additional NFAs derived from perylene diimide (PDI) dimers were investigated. The first PDI₂Ac₂ (**Pa2**) was synthesized by connecting two PDI monomers with a double acetylene bridge. The second DPP-(Ac-PDI)₂ (**DaP2**) is obtained by a synthesis of diketopyrrolopyrrole (DPP) connected to the two molecules of PDI by an acetylene bridge on each side. DPP based materials have been so far investigated for their excellent charge carrier mobilities and fluorescent properties. The third acceptor was based on thienoisoindigo (TII) and acetylene (**TaP2**), which serves as the linker moiety between the PDI dimers, based on that earlier representative derived from thienoisoindigo have shown good optical properties and charge carrier mobilities but have not been appropriately investigated in OSC applications. The schematics of all materials used for this study are given in **Figure 1**.

Electrochemical characterization

To match the energy levels in organic photovoltaic devices, it is essential to determine the HOMO and LUMO onsets of the donor and acceptor components. Cyclic voltammetry (CV) is a powerful tool to determine the HOMO and LUMO energy of organic elements. The ionization

potential (HOMO) level and electron affinity (LUMO) level can be estimated from oxidation and reduction onset potentials on the basis of a redox reference such as ferrocene (5.0 eV below the vacuum level) (Namazian et al. 2010).

$$E_{\text{HOMO}} = - ((E_{\text{ox}})_{\text{onset}} + \text{potential of Fc/Fc}^+ \text{ couple}) \text{ eV}$$

$$E_{\text{LUMO}} = - ((E_{\text{red}})_{\text{onset}} + \text{potential of Fc/Fc}^+ \text{ couple}) \text{ eV}$$

The HOMO and LUMO values were evaluated from the first oxidation and reduction peak onsets of the CV, the measurements were performed on a VMP3 potentiostat (Biologic, France) using a standard three-electrode setup with a glassy-carbon disk working electrode (diameter 2 mm), a AgNO₃/Ag/CH₃CN reference electrode and a platinum wire counter electrode. The measurements were conducted in chloroform (spectroscopic grade) containing 0.1 M Bu₄NPF₆ as conducting salt and ca. 1 mg·mL⁻¹ of the sample. The solutions were de-aerated *via* purging with argon prior to each measurement. The applied scan rate was 200 mV·s⁻¹.

Optical characterization

Contactless and non-destructive thin film steady-state photoluminescence (PL) spectra were recorded with an AvantesAvaSpec ULS-2048 fiber spectrometer. PL excitation was conducted with a laser diode emitting at 405 nm. For PL correction of absorption and evaluation of optical band-gaps, thin film transmission and reflection spectra were recorded with two Avantes AvaSpec-ULS3648-USB2-UA-25 fiber spectrometers reassembled to the thin film absorption spectra.

Atomic Force Microscopy (AFM)

To gain further insight into the morphology of the blends system, AFM measurements were performed in tapping mode on a NTEGRA Aura (NT-MDT) using tapping mode cantilevers from Mikromasch (NSC35).

I-V characterization

Photovoltaic devices of conventional and inverted architecture were studied under dark and AM1.5 conditions. The current–voltage (IV) measurements of the solar cell devices were recorded with a Keithley 2400 Source-Meter-Unit (SMU). The intensity of the light source was calibrated by a standard silica photodiode to confirm AM1.5 condition and the intensity of 100 mW/cm². The details of the solar cells preparation and layer stacks were explicated in the experimental section.

Time-Delayed Collection Field (TDCF)

TDCF is a pump-probe technique, and the analyses that are particularly relevant to the study of field dependence of charge generation, charge extraction, and charge recombination dynamics in solar cells (Albrecht et al. 2012; Kniepert et al. 2014; Kniepert et al. 2011). The home-built TDCF setup uses the second harmonic (532 nm) of an actively Q-switched sub-ns Nd:YVO₄ laser (InnoLas piccolo AOT) operating at 5 kHz as excitation. In order to minimize the RC response time, a small device area of 1mm² was used. The samples were measured under dynamic vacuum conditions to avoid any degradation. 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.

Preparation of films and BHJ OSCs

The global polymer and acceptors weight ratio was held constant at 2:3. **AnE-PVstat** and the acceptor materials were dissolved in a 1:1 (vol %) solvent mixture of chlorobenzene and chloroform (CB:CF) as found to be the optimal mixture promoting phase separation *via* aggregation in **AnE-PVstat:PCBM** blends (Kastner et al. 2015; Kastner et al. 2013). However, the solvent systems were not optimized for non-fullerene acceptors. 12 mg/mL polymer and 18 mg/mL of acceptor were prepared separately. In order to have 2:3 blend ratio of polymer (12 mg/mL):acceptor (18 mg/mL) was blended together in 1:1 ratio from the pristine solutions. The

films were casted from pristine and blended solution onto glass for optical measurements. Blended solutions were coated as active layer of OSC.

Figure 2: Schematic representation of the conventional (left) and inverted (right) polymer solar cell layer stacks.

For fabrication of the OSC, two different layer stack architectures were used. The fabrication of OSC started with cleaning the glass/indium tin oxide (ITO) substrates in ultrasonic bath successively using acetone and isopropanol for 15 min each. In the case of conventional architecture, poly(3,4ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) was spin-casted from aqueous solution on top of ITO at 3000 rpm for 35 seconds as the hole transporting layer (HTL). The substrates were then annealed on a hot plate for 15 minutes at 180°C in order to remove the residual water content from the films. Afterward, the samples were transferred to the glovebox (N₂) immediately and cooled down to room temperature. Active layer solutions were casted on top of the PEDOT:PSS layer with 600 rpm spin frequency and run for 45 seconds. Later on the films were transferred to the vacuum chamber in order to deposit the top electrode. Solar cells were finished with thermal evaporation of 50 nm of magnesium and 100 nm of aluminum (Al) deposited sequentially through a shadow mask as an electron collecting electrode giving 0.42 cm² active area of the solar cells. To build inverted solar cells, polyethyleneimine (PEI)/TiO_x blends were spin casted on cleaned ITO substrate and these devices were completed with 10 nm molybdenum trioxide (MoO₃) and 100 nm silver (Ag) through a shadow mask. 0.27 mg/ml PEI is diluted in Butanol and 1.5 vol% TiO_x in Isopropanol are blended with the ratio of 1:1 (vol %). PEI and TiO_x blends are spin-coated on top of the ITO at 3000 rpm for 30 seconds. Thin layer of PEI/TiO_x was annealed at 105°C for 5 min inside the glove-box. Photoactive layers were kept the same as in conventional architecture. All the OSCs were sealed under glass using UV-curing glue (epoxy-based) inside the glove box. Conventional and inverted architectures are shown in **Figure 2**.

Results and Discussion

In order to elucidate the energy alignment and compatibility of the **AnE-PVstat** polymer with different non-fullerene acceptors, CV measurements were performed on pristine materials. In case of **AnE-PVstat**, we can see a first oxidation wave at $E_{\text{onset}} = 0.25$ V, a second one, which leads to subsequent irreversible reactions (most likely electro-polymerization), and a reduction signal at $E_{\text{onset}} = -1.24$ V were obtained. We note that the latter two signals are electrochemically irreversible. However, all the non-fullerene acceptors show quasi-reversible oxidation signals. And **ITIC** showed an electrochemically irreversible reduction signal at $E_{\text{onset}} = -1.04$ V. In contrast; all the PDI-based non-fullerene acceptors exhibited quasi-reversible reduction signals. **Figure 3** illustrates the CV curves of **AnE-PVstat**, **PCBM**, **ITIC**, **Pa2**, **DaP2**, **TaP2**, in detail oxidation and reduction onset values are presented in the graph.

Figure 3: CV curves of **AnE-PVstat** , **PCBM**, **ITIC**, **Pa2**, **DaP2** and **TaP2**, oxidation and reduction onsets are presented in the graph.

Bandgap energies were calculated from the HOMO-LUMO difference. **Table 1** summarizes the electrochemical data obtained from the CV measurements. The expected energy level alignment in type II heterojunctions can be estimated from **Figure 4**.

Table 1: Oxidation and reduction onset potentials from CV measurements, calculated HOMO, LUMO energies for the pristine polymer and different acceptor materials as well as their electrochemical and optical (see below) bandgaps and their difference are summarized.

Material	Oxidation onset		Reduction onset		HOMO (eV)	LUMO (eV)	Electrochemical bandgap $E_{G,EC}$ (eV)	Optical bandgap $E_{G,O}^*$	$\Delta E_G = E_{G,O} - E_{G,EC}$
	1 st	2 nd	1 st	2 nd					
AnE-Pvstat	0.25		-1.24		-5.25	-3.76	1.49	1.92	0.43
PCBM	1.10		-1.10		-6.10	-3.90	2.20	2.33	0.13
ITIC	0.71	1.07	-1.04		-5.71	-3.96	1.75	1.45	-0.30
Pa2	1.10		-1.09	-1.43	-6.10	-3.91	2.19	1.94	-0.25
DaP2	0.53		-1.11	-1.36	-5.53	-3.89	1.64	1.50	-0.14
TaP2	0.43		-1.12		-5.43	-3.88	1.55	1.33	-0.22

Figure 4: HOMO-LUMO energy levels, respectively bandgaps, of **AnE-PVstat** , **PCBM**, **ITIC**, **Pa2**, **DaP2** and **TaP2** are depicted.

Thin films of **AnE-PVstat:PCBM** and **AnE-PVstat:NFA** blends on glass substrates were processed from solution at room temperature under inert (N_2) environment. These samples were used in spectroscopic and morphology studies. The obtained absorption and photoluminescence spectra are shown in **Figure 5**.

Figure 5: Absorption (left hand side) and photoluminescence (right hand side) spectra for **AnE-PVstat**, **PCBM** and various NFA's, in pristine films and blends.

Pristine **AnE-PVstat** donor, pristine acceptors and blends thereof are compared in absorption and PL. On the left-hand side of **Figure 5**, absorption spectra of the pristine **AnE-PVstat**, pristine acceptors, and their blends are shown. **DaP2** and **TaP2** show a complimentary absorption to **AnE-PVstat** increasing the absorption range, while **Pa2** only slightly adds some absorption towards longer wavelengths to the blend with **AnE-PVstat**. Optical band gaps are extracted from the intersection between the absorption and PL spectrum of pristine materials for comparison with electrochemical band gaps. The values of the optical band gap (E_g) and the difference with respect to electrochemical gaps are shown in **Table 1**.

In order to compare the PL intensities from the thin film samples, the recorded PL spectra have been normalized with respect to the absorption at the excitation wavelength of the laser (405 nm). On the right hand side of **Figure 5**, the PL spectra of pristine **AnE-PVstat**, pristine acceptors, and their blends are shown. From the PL spectra of the **AnE-PVstat:PCBM**, we can deduce that the polymer PL is noticeably quenched, the quenching factor is ~ 110 . According to the PL results, **AnE-PVstat:NFA's** blends may be so finely intermixed that grain sizes become too small and thus PL signals are quenched.

The PL intensity of pristine **AnE-PVstat** and **ITIC** in films are more or less same; however polymer intensity is completely quenched in the blend. A PL spectrum of **Pa2** is similar to **AnE-PVstat**. However the polymer PL is quenched and we could only see the acceptor PL in the blend. In case of **DaP2** and **TaP2**, strong quenching of all PL signals upon blending with **AnE-PVstat** is found. We can conclude from the PL studies that there are sufficient energy level offsets for electron transfer. The energy transfer could occur for **ITIC**, **DaP2**, and **TaP2** as the optical absorption overlaps with the emission of the polymer donor.

Figure 6: Tapping mode AFM images (area $2.5 \times 2.5 \mu\text{m}^2$) are shown for **AnE-PVstat:PCBM** and **AnE-PVstat:NFA's** blends.

AFM measurements were conducted on the same films that were used for optical characterization are shown in **Figure 6**. The AFM images show that in case of **PCBM** and **ITIC**,

there is a slightly larger average grain size, which may be associated with the **AnE-PVstat** phase. Such a larger phase separation may yield more favorable charge percolation pathways than for the remaining non-fullerene acceptors. The smaller apparent domain sizes are in good agreement with complete polymer PL quenching. Although AFM topography images do not afford adequate in-depth information about the blend morphology for PDI based NFA's with **AnE-PVstat**, the most straightforward assumptions are no changes within the blend organization occur in the depth of the film. This leads finely scaled surface morphology due to the homogeneously intermixed bulk structure.

Figure 7 illustrates dark (left) and light (right) I-V curves of the solar cells prepared in conventional and inverted architectures. In case of conventional architecture, only blends with **PCBM** exhibit a decent diode characteristic in the dark. The remaining blends show symmetric characteristics. Although, when recorded under solar simulation, a somewhat increased current was found for all blends, the currents remained more or less symmetric – but now around the open circuit voltage for blends with NFA's. Alone **AnE-PVstat:PCBM** blends exhibited the required photovoltaic characteristics.

In case of inverted devices, the situation became even more remarkable, while for **PCBM** the diode characteristics improved even further, leading to a higher rectification than for the conventional architecture, specifically the **DaP2** and **TaP2** exhibited shallow currents within the ohmic regime. However, under forward bias diode characteristics could be observed in all cases, though differently well developed. In general, lower photocurrents were obtained for inverted devices but somewhat increased open circuit voltages were found for all NFA-based blends. **Table 2** shows the summary of the photovoltaic parameters of the solar cells devices of conventional and inverted architecture.

Figure 7: Top-left: logarithmic dark I-V curves of conventional solar cells, top-right: logarithmic I-V curves of conventional solar cells under illumination. Bottom-left: logarithmic dark I-V curves of inverted solar cells, bottom-right: logarithmic I-V curves of inverted solar cells under illumination.

Table 2: Photovoltaic parameters from solar cells devices of conventional and inverted configuration

Materials	Solar cell type	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)	η (%)	R_S (Ohm)	R_P (kOhm)
AnE-PVstat:PCBM	Conv.	7.951	830	53	3.48	26	2.4
AnE-PVstat:ITIC	Conv.	0.396	612	28	0.07	2332	4.4
AnE-PVstat:Pa2	Conv.	0.038	127	25	<0.01	5297	8.1
AnE-PVstat:DaP2	Conv.	0.004	50	24	<0.01	25095	28.4
AnE-PVstat:TaP2	Conv.	0.005	57	25	<0.01	4359	27.2
AnE-PVstat:PCBM	Inv.	6.824	795	36	1.97	181	0.64
AnE-PVstat:ITIC	Inv.	0.359	895	29	0.09	3267	6.7
AnE-PVstat:Pa2	Inv.	0.091	900	32	0.03	347	34.3
AnE-PVstat:DaP2	Inv.	0.007	739	39	<0.01	1645	471.6
AnE-PVstat:TaP2	Inv.	0.007	655	36	<0.01	1544	388.1

In order to clarify the origin of low photocurrents, time-delayed collection field (TDCF) measurements were performed on **AnE-PVstat:PCBM**, **AnE-PVstat:ITIC** and **AnE-PVstat:Pa2** based solar cells in conventional device architecture. Systems that suffer from field-dependent generation, show a strong dependence of the amount of charges generated on the applied electric field, which decreases towards the open circuit voltage, typically leading to low fill factors (Howard et al. 2014) and suffering both geminate and non-geminate recombination, while systems with field-independent charge generation only suffer from non-geminate recombination.

Figure 8: The TDCF data reveals field independent charge generation in **AnE-PVstat:PCBM**, **AnE-PVstat:ITIC** and **AnE-PVstat:Pa2** solar cells. The sample measured were prepared in conventional architecture

In the present case, low excitation fluence was chosen, to avoid non-geminate recombination losses prior to charge extraction. The total number of charges, namely Q_{tot} , generated in the solar cells under these low fluence conditions, is thus a direct measure of the amount of free charge generated by the excitation laser pulse as a function of the applied pre-bias. The measured Q_{tot} as a function of the applied pre-bias during photoexcitation, after a delay time of 10 ns is shown in **Figure 8**.

Figure 9: Delay-time charge collection measurements data for **AnE-PVstat:PCBM**, **AnE-PVstat:ITIC** and **AnE-PVstat:Pa2** solar cells

In **Figure 8**, the open squares denote Q_{tot} from TDCF measurements. The area above the symbols and below the J-V curve (blue line) indicates losses caused by non-geminate (bimolecular) recombination. Charge generation is field-independent in the case of **AnE-PVstat:PCBM** and **AnE-PVstat:ITIC** devices, suggesting that significant loss in these systems are non-geminate recombination. Because of the low current density in the **AnE-PVstat:Pa2** device, the Q_{tot} is widely scattered, and does not show a clear trend. It is worth noting that the geminate recombination of CT-states, which do not separate under the low pre-bias applied in TDCF experiments cannot be detected here. To get access to the charge recombination rate, time delayed charge collection measurements were performed is shown in **Figure 9**. All samples were kept at V_{oc} , and a low fluence of $4 \mu\text{J}/\text{cm}^2$ was chosen. The recombination rate, namely r , was extracted based on fitting to the following equation (Kniepert et al. 2011).

$$q_{coll}(t_d + \Delta t) - q_{coll}(t_d) = -[q_{pre}(t_d + \Delta t) - q_{pre}(t_d)] - \gamma \frac{q_{coll}^2(t_d)}{eAd} \Delta t$$

The recombination rates for the three measured systems were 2.9×10^{-12} , 2×10^{-11} , and $3.6 \times 10^{-10} \text{ cm}^3/\text{s}$, for **AnE-PVstat:PCBM**, **AnE-PVstat:ITIC** and **AnE-PVstat:Pa2** based solar cells respectively. The recombination rate is massively enhanced in case of NFA's by one and two orders of magnitude, for **ITIC** and **Pa2**, respectively.

Conclusion

In summary, while the moderate performance of organic bulk heterojunction solar cells was obtained for the PPE-PPV copolymer donor combined with the classical fullerene acceptor **PCBM**, poor performance was found for blends with novel non-fullerene acceptors. Photoluminescence quenching measurements and atomic force microscopy indicated a too fine intermixing of donor and acceptor components. While this alone does not explain the poor photocurrents, strongly increased charge recombination rates were found in case of non-fullerene acceptors *via* TDCF measurements. Overall, the poor performance of **AnE-PVstat** combined with NFA's has to be assigned to both, insufficient charge generation and increased charge recombination *via* non-geminate recombination. The origin of low charge generation yields is currently subject of further studies. This study demonstrates the relative ease of obtaining moderately well-performing fullerene-acceptor based polymer solar cells, while NFAs may require further optimization before they can be successfully matched with existing donor polymers.

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