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Design of Narrow Bandgap Non-Fullerene Acceptors for Photovoltaic Applications and Investigation of Non-Geminate Recombination Dynamics

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This paper is dedicated to Professor Tobin Marks on the occasion of his 75th birthday.

Keywords: organic photovoltaics, non-fullerene acceptors, near-infrared optoelectronics, narrow bandgap acceptors, non-geminate recombination

Abstract

A new narrow bandgap non-fullerene electron acceptor was designed, synthesized, and characterized for near-infrared organic photovoltaics. This acceptor was compared to a structurally similar compound with systematically modified side chains, and a series of solar cells were fabricated, employing the common donor polymers PTB7-Th and PBDBT. The devices exhibited charge generation over a wide spectral range and power conversion efficiencies up to 8.1 %. The non-geminate recombination dynamics were investigated and quantified *via* a combination of capacitance spectroscopy and transient open-circuit voltage decay measurements. The reduction of the bandgap results in increased bimolecular recombination losses, while solar cells composed of PBDBT were afflicted by stronger monomolecular, i. e. trap-assisted, recombination losses that ultimately caused the lower power conversion efficiencies of the respective devices. The latter observation could be correlated to less ordered blend film morphology.

1. Introduction

In recent years, organic photovoltaics (OPVs) have received increasing attention owing to the potential of manufacturing large-area, flexible solar cells *via* mild and economically favorable solution-based processing techniques.[1, 2] The gains in performance recently observed for OPVs can mostly be attributed to the use of non-fullerene acceptors (NFAs) that were developed through continuous efforts to replace the hitherto ubiquitous fullerene-based acceptors.[3, 4] Organic solar cells (OSCs) based on fullerene acceptors in a bulk-heterojunction (BHJ) configuration yield power conversion efficiencies (PCEs) of up to 11 % for single-junction devices,[5, 6] while PCEs of over 17 % have been reported for state-of-the-art, single-junction and tandem NFA-OSCs, placing them within reach of the performance range of perovskite solar cells.[7-9] In addition to the increased performance, NFAs can be tuned to yield compounds that absorb at longer wavelengths (e.g., near-

infrared).[10, 11] This control over the bandgap opens up the potential to develop semi-transparent OSCs that could find application in building-integrated photovoltaics and in agriculture.[12, 13] Even when considering the recent advances in NFAs, it is still necessary to develop a deeper understanding of loss mechanisms in NFAs such as non-radiative and non-geminate recombination – the process where free electrons and holes originating from different excitons recombine – to further improve the performance of OSCs.[14-18] This is especially required since the interplay between narrow bandgap NFAs ($E_g \leq 1.3$ eV) and polymers such as PTB7-Th or PBDBT, originally designed for fullerene acceptors,[19, 20] is yet not fully understood.[21, 22] Hence, this study focuses on four different narrow bandgap blend systems in solar cells, the observed photo-physical, morphological, and OPV performance differences, and how these differences relate to the non-geminate recombination dynamics.

2. Results and Discussion

We recently reported narrow bandgap electron acceptors, namely CTIC-4F and COTIC-4F, which are characterized by optical bandgaps (E_g^{opt}) of 1.3 and 1.1 eV, respectively.[11, 23] The molecules are designed based on an A−D'−D−D'−A molecular configuration, consisting of cyclopentadithiophene (CPDT) as the central donor (D) unit, thienyl units as the flanked sub-donor (D') fragments, and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile as the terminal acceptor (A) units. The molecular structures of CTIC-4F and COTIC-4F differ by their side chains on the D' fragments, specifically alkyl vs. alkoxy groups for CTIC-4F vs. COTIC-4F. Changing the substituent of side chains on the thienyl fragments is an effective way to modulate the frontier orbital energy levels and absorption profiles of organic semiconductors.[24, 25] In this work, we designed a new NFA derivative, namely CETIC-4F (Figure 1), containing a carboxylate substituted group in the 3-position of the D'-thienyl unit (see Scheme S1, Figures S1-S4). As evidenced by the optical

transitions and the cyclic voltammetry, incorporating electron-withdrawing carboxylate substituents into alkyl side chains lowers the HOMO level from −5.36 eV for CTIC-4F to −5.47 eV for CETIC-4F, while resulting in a minor effect on the optical bandgap (Figure 1, Figure S5). This underlines the potential of the aforementioned synthetic strategy to finely tune the NFAs for energy level matching, while maintaining a similar bandgap.

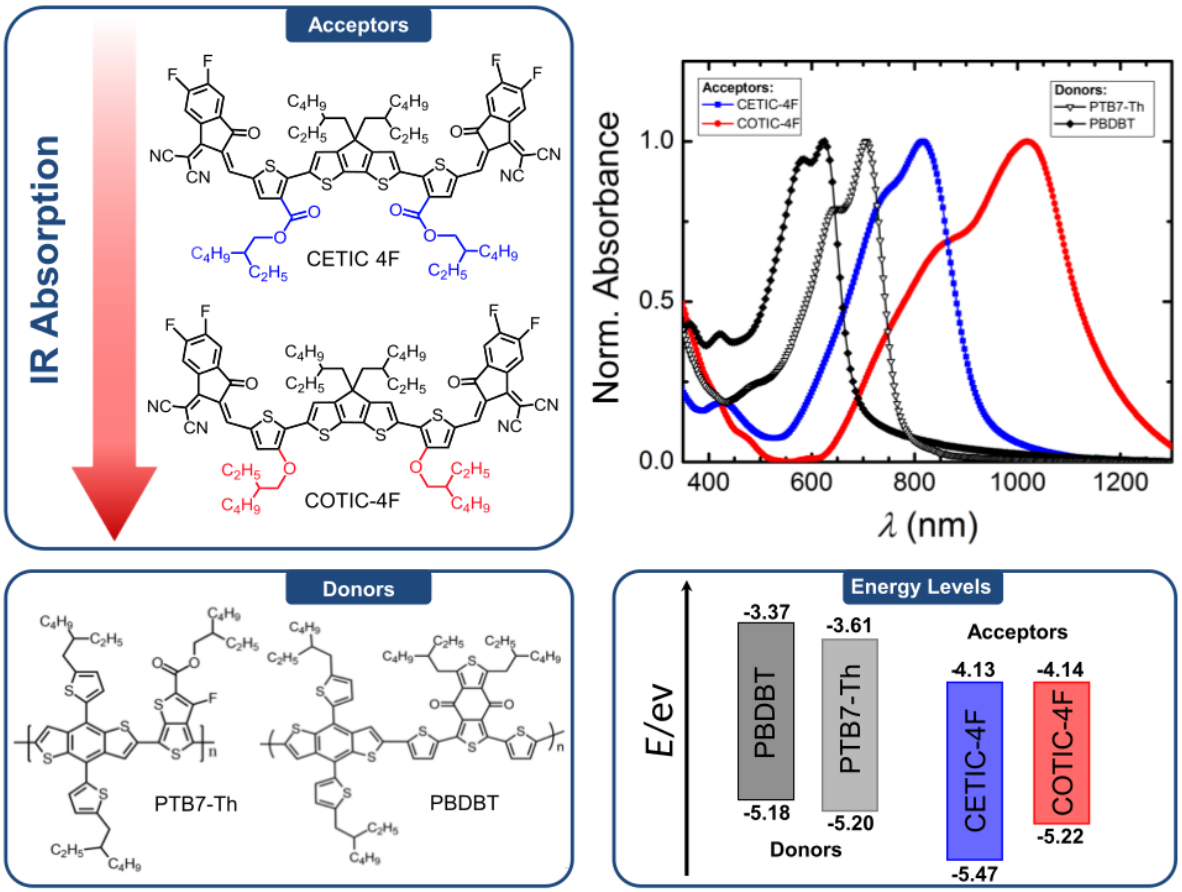

Figure 1. Chemical structures of the studied non-fullerene acceptors and donor polymers, absorption spectra of pristine thin films, and relevant energy levels.

Organic solar cells were fabricated and optimized to investigate the photovoltaic performance of two donors and two NFAs, namely PBDBT and PTB7-Th[19, 20, 26] as well as CETIC-4F and COTIC-4F (see ESI).[11, 23] The same trend in performance can be observed for the two sets of devices with different donors, where of the investigated NFAs, CETIC-4F shows the highest PCE compared to COTIC-4F (see Figure 2, Table 1). Furthermore, the devices with PTB7-Th as the donor perform better than their PBDBT counterparts, owing to higher values of

the short-circuit current density (J_{SC}) and fill factor (*FF*), while in contrast the open-circuit voltages (V_{OC}) tend to be of a similar value. The COTIC-4F devices showed the biggest drop in PCE when changing the donor polymer, namely from up to 7.04 % (PTB7-Th:COTIC-4F) to only 2.32 % (PBDBT:COTIC-4F). The external quantum efficiency (EQE) measurements reveal that PTB7-Th:CETIC-4F and PBDBT:CETIC-4F devices show charge carrier generation in the spectral range of 300 – 950 nm, while PTB7-Th:COTIC-4F and PBDBT:COTIC-4F devices exhibit charge generation at even longer wavelengths (300 – 1100 nm), which is in good agreement with the thin film absorption spectra and earlier reports (Figures 1 and 2).[11] Furthermore, the photocurrent density (J_{ph}) was calculated, which is defined as follows:

$$J_{ph} = J_{light} - J_{dark}, \quad (1)$$

where J_{light} is the current density under illumination and J_{dark} is the current density in the dark (see Figures S6 and S7). The photocurrent density can be compared between the different devices by plotting against the effective voltage $V_{eff} = V_0 - V_{cor}$, where V_0 is the voltage at which $J_{ph} = 0$ (Figure 2) and V_{cor} is the applied voltage corrected for the losses caused by the series resistance ($V_{cor} = V_{app} - J \cdot R_{series}$).[27, 28] Similarly, the probability of charge collection P_C is accessible from the ratio between the saturated photocurrent density $J_{ph,sat}$ with the values for J_{ph} at different biases:[29]

$$P_C = \frac{J_{ph}}{J_{ph,sat}}. \quad (2)$$

As can be seen in Figure S8, the PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F devices exhibit a better charge collection P_C than their PBDBT counterparts. When the two NFAs are compared, PTB7-Th:CETIC-4F and PBDBT:CETIC-4F devices show a higher P_C than PTB7-Th:COTIC-4F and PBDBT:COTIC-4F devices, respectively; this difference is subtle for the PTB7-Th devices, while significant for the PBDBT devices. Ultimately, a reasonable correlation between the collection probability P_C and the device performance can be observed, where higher values for P_C, specifically at forward bias around maximum-power conditions, go hand in hand with higher

values for the solar cell PCEs. Additionally, *J*-*V*-curves at varying light intensities were measured to qualitatively inspect the non-geminate recombination mechanisms (Figure S9). The measured J_{SC} and the light intensity I follow a power law ($J_{SC} \propto I^{\alpha}$) and exhibit similar values for the exponent ($\alpha \approx 0.9$). Bimolecular recombination and space charge effects resulting from imbalanced hole and electron mobility can both be responsible for such an observation. Indeed, the hole and electron mobility ($\mu_{h,e}$) obtained *via* single-carrier diodes analyzed *via* the Mott-Gurney relationship show significant differences in the magnitude of the two types of mobility for all systems ($\mu_h/\mu_e = 5 - 138$, Figure S11 and Table S2). It is therefore likely that the deviation of the exponent α from unity is caused by the aforementioned space charge effect rather than by the influence of bimolecular recombination alone.[30, 31] The second common approach to investigate the types of non-geminate recombination mechanisms of solar cells is by determining the relationship between the V_{OC} and the light intensity *I*:[32, 33]

$$V_{OC} \propto \frac{kT}{q} ln(I), \quad (3)$$

where k is the Boltzmann constant, T is the absolute temperature ($T = 300$ K), and q is the elementary charge.[34] The V_{OC}-ln(I)-plots exhibit a slope of $S = 1\ kT/q$ for solar cells in the case of ideal, pure bimolecular recombination. However, the presence of bulk or surface traps can cause monomolecular recombination that lead to deviations of the slope (bulk traps: $S > 1\ kT/q$; surface traps: $S < 1\ kT/q$).[22, 35, 36] The V_{OC}-ln(I)-plots exhibit good linearity over the investigated light intensities and the slopes determined for the studied devices are in a range of $S = 0.84 - 1.13\ kT/q$. These results indicate that all types of non-geminate recombination should be taken into account as loss mechanisms.[36] Hence, the light intensity dependent *J*-*V*-curves are not sufficient to paint a conclusive picture of the non-geminate recombination dynamics and a more in-depth analysis is necessary to obtain quantitative results.

Table 1. Photovoltaic performance of OSCs with blends consisting of PBDBT or PTB7-Th as donor and CETIC-4F and COTIC-4F as acceptor, measured at simulated 100 mW/cm^2 AM 1.5G illumination.

Donor	NFA	V_{OC} [V]	J_{SC} [mA/cm^2]	FF	PCE$_{avg\ (max)}$ [%][c)]	$J_{SC,calc}$ [mA/cm^2][d)]	EQE$_{max}$ [%]
PBDBT[a)]	CETIC-4F	0.71 ± 0.01	15.6 ± 1.1	0.54 ± 0.03	5.96 ± 0.77 (6.59)	15.72	58
	COTIC-4F	0.55 ± 0.03	8.0 ± 0.3	0.49 ± 0.01	2.19 ± 0.12 (2.32)	7.78	26
PTB7-Th[b)]	CETIC-4F	0.65 ± 0.01	19.1 ± 1.0	0.61 ± 0.03	7.61 ± 0.33 (8.08)	18.66	72
	COTIC-4F	0.56 ± 0.01	20.2 ± 0.9	0.59 ± 0.01	6.66 ± 0.17 (7.04)	20.40	57

[a)]PBDBT:NFA blend ratio: 1:1 (w/w); [b)]PTB7-Th:NFA blend ratio: 1:1.5 (w/w); [c)] Average values from 10 devices; [d)]J_{SC} calculated from EQE measurements

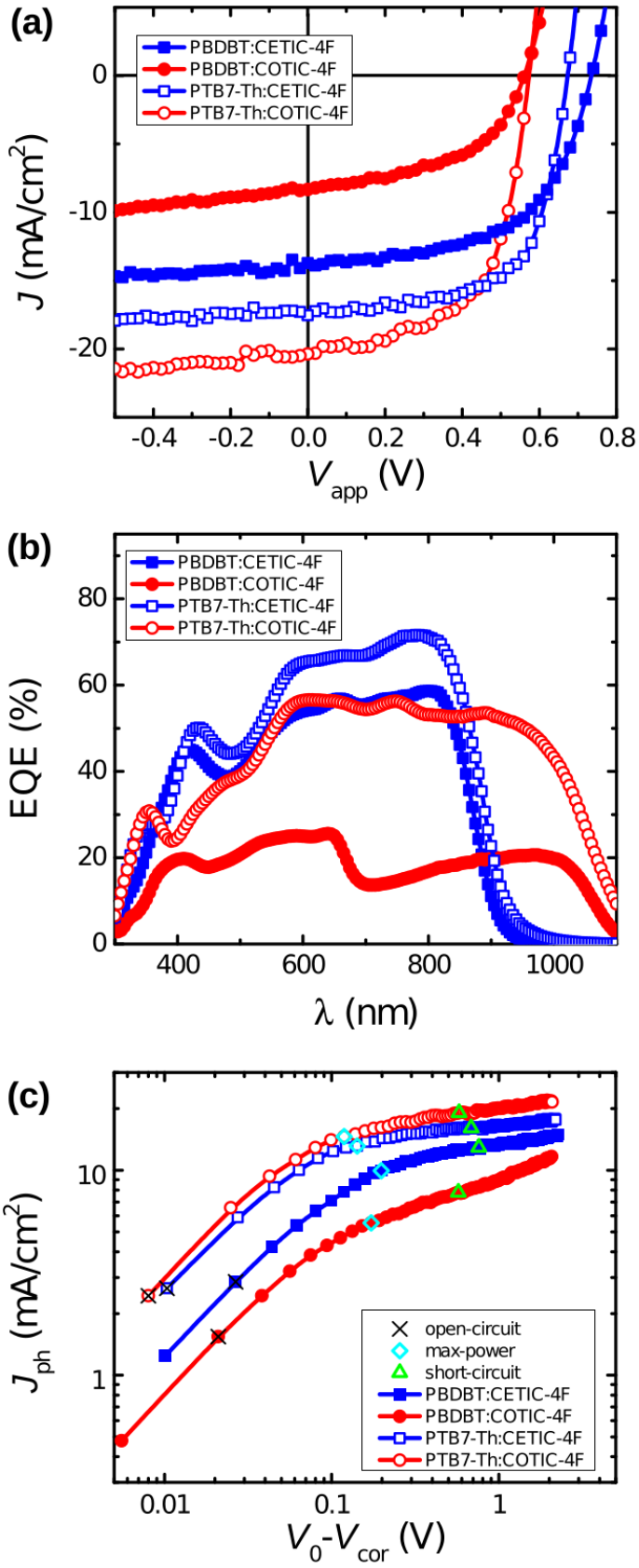

Figure 2. (a) *J*-*V*-characteristics, (b) EQE, and (c) photocurrent density J_{ph} as a function of the effective voltage V_0-V_{cor} of the studied solar cells. Operating conditions of interest such as open-circuit, max-power, and short-circuit are highlighted for convenience.

The recombination dynamics in the studied solar cells were quantified *via* an analysis based on capacitance spectroscopy that allows the determination of the charge carrier density n (Equations S3-S5, Figure S12, Figure 3a).[37] The studied solar cells show charge carrier densities in a similar range, with the biggest divergence at forward bias approaching open-circuit conditions (highest for PTB7-Th:CETIC-4F: $n = 5.2 \cdot 10^{16}$ cm^{-3}; lowest for PBDBT:CETIC-4F: $n = 2.6 \cdot 10^{16}$ cm^{-3}). To obtain a quantitative understanding of the recombination mechanisms, it is assumed that the overall measured recombination current density ($J_{rec} = J_{ph,sat} - J_{ph}$) is a superposition of the three aforementioned recombination mechanisms that contribute a certain part to the total recombination current density J_{rec}:

$$J_{rec} = J_{bm} + J_{tb} + J_{ts} = qL\left(\frac{n}{\tau_{bm}} + \frac{n}{\tau_{tb}} + \frac{n}{\tau_{ts}}\right) = qL(k_{bm}n^2 + k_{tb}n + k_{ts}n), \quad (4)$$

where q is the elementary charge, L is the active layer thickness, τ is the charge carrier lifetime, n is the charge carrier density, and k is the recombination coefficient of the three different recombination mechanisms (bm: bimolecular; tb: bulk trap-assisted; ts: surface trap-assisted). By reconstructing the recombination current density J_{rec} obtained from the *J-V*-curves with the charge carrier density (n) and the effective mobility (μ_{eff}), which is explained in the ESI, it is possible to quantify the recombination coefficients (k) (Figures S13-S15).[22, 38] In general, the PTB7-Th:COTIC-4F and PBDBT:COTIC-4F devices exhibit higher bimolecular recombination coefficients k_{bm} than their CETIC-4F-based counterparts. Furthermore, the fitting yields higher contributions of bulk trap-assisted recombination in the PBDBT:CETIC-4F and PBDBT:COTIC-4F devices compared to the PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F solar cells, which could be the reason for the reduced performance of the PBDBT OSCs (Figures S15). In addition, the contributions of surface trap-assisted recombination are only relevant under open-circuit conditions for all tested devices and even under these conditions they do not dominate the non-geminate recombination dynamics (Figure S14).

In a subsequent step, it is possible to calculate the charge carrier lifetime τ_{rec} by rearranging equation (4), since the carrier density n and the relevant recombination coefficients (k_{bm}, k_{tb}, k_{ts}) are now known (Figure 3b). However, it is necessary to also take the extraction dynamics of the investigated solar cells into account to obtain a complete picture, since non-geminate recombination and extraction are in a direct competition to each other (see Equations S6-S8).[21, 39] To this end, the effective extraction time τ_{ex} can be defined as follows:

$$\tau_{ex} = \frac{qLn}{J}, \quad (5)$$

where q is the elementary charge, L is the active layer thickness, n is the charge carrier density, and J is the current density (Figure 3b).[38] Once the charge carrier lifetime and the extraction time are determined, it is possible to calculate the competition factor ($\theta = \tau_{ex}/\tau_{rec}$), a figure of merit introduced by Barthesaghi et al. in 2015.[39] In this study, the bias-dependent competition factor θ is accessible, since the bias-dependent lifetime and extraction time were determined.[38] In summary, a good reciprocal relationship between the competition factor θ and figures of merit for the device performance (*FF*, *PCE*) can be observed (Table 2), where lower θ values go hand in hand with a higher device performance.

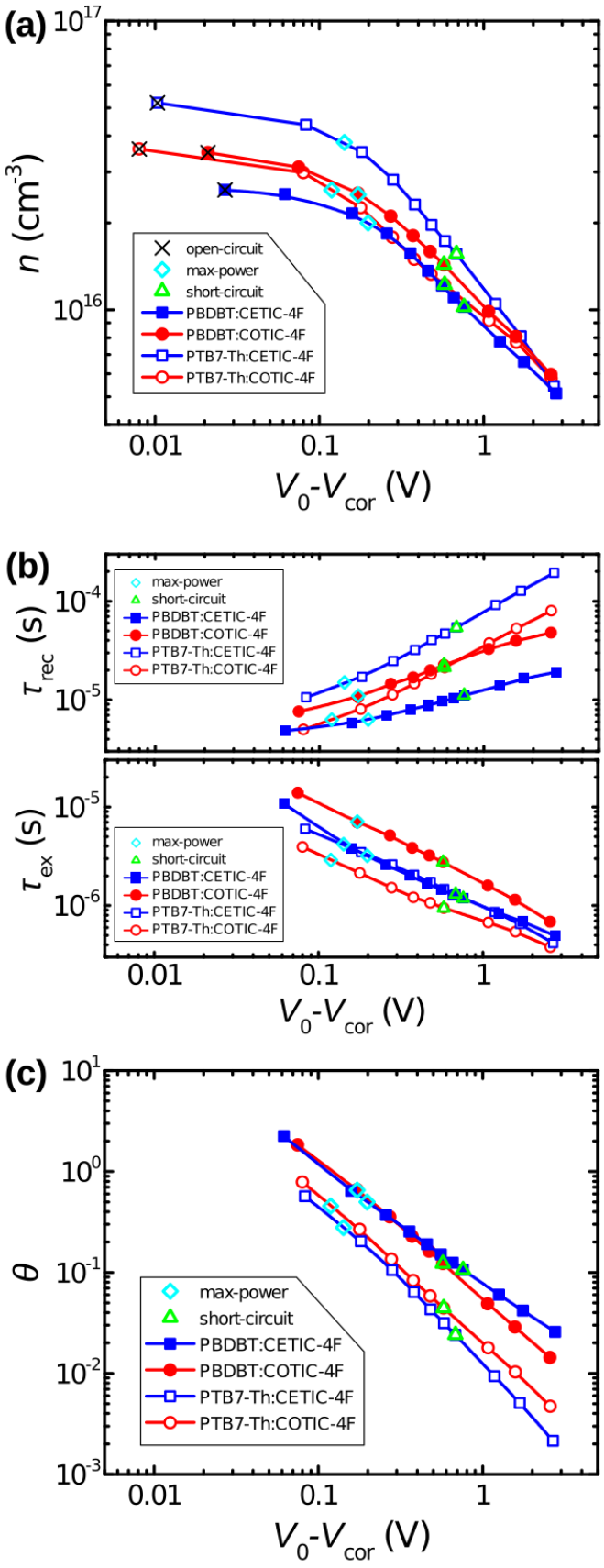

Figure 3. (a) Charge carrier density n, (b) recombination lifetime τ_{rec} as well as extraction time τ_{ex}, and (c) competition factor θ as a function of the effective voltage V_0-V_{cor} of the studied solar cell determined *via* capacitance spectroscopy. Operating conditions of interest such as max-power, and short-circuit are highlighted for convenience.

In addition to the analysis based on capacitance spectroscopy, we also performed transient open-circuit voltage decay measurements on the solar cells as a secondary method to investigate the relevant non-geminate recombination processes (see Equations S9-S14 and Figure S16). The V_{OC}-transients depicted convey significant differences between the PTB7-Th and PBDBT devices (Figure 4a). It takes up to one order of magnitude longer for the V_{OC} to drop to half of its initial value for PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F devices ($t_{½}$ = 0.6 – 1.2 ms), when compared to their PBDBT:CETIC-4F and PBDBT:COTIC-4F counterparts ($t_{½}$ = 0.06 – 0.13 ms; Table 2), which is suggestive of higher recombination rates in the PBDBT devices. The carrier lifetime τ_{rec} and the recombination order β can be determined from the transients of the V_{OC} for the relevant timescales not dominated by the shunt resistance limit (PTB7-Th devices: $t < 10^{-3}$ s; PBDBT devices: $t < 10^{-4}$ s, Figure S16). It is revealed that the highest recombination order β_{max} reached for the PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F devices ($\beta_{max} \approx 1.6$) is larger than for the PBDBT:CETIC-4F and PBDBT:COTIC-4F devices ($\beta_{max} \approx 1.4$) (Equations S11-S14, Figure S16, and Table 2). Another interpretation of the recombination order β is as an indicator of the relative contribution to the effective recombination by bimolecular and/or monomolecular recombination.[40] Therefore, higher values of β_{max} result either from an increased bimolecular contribution, a decreased trap-assisted (e.g. monomolecular) contribution, or a combination of both cases. To fully quantify the recombination, it is necessary to transform the measured V_{OC} values to the transient charge carrier density n_{OC} and plot the carrier lifetime τ_{rec} against it (Figure 4b,c). Furthermore, it has to be stressed that bulk and surface trap-assisted recombination cannot be distinguished by this method.[22] The analysis to obtain the transient carrier density n_{OC} and the lifetime τ is described in detail in the ESI (Equations S11-S14). In essence the carrier densities under open-circuit conditions determined *via* capacitance spectroscopy act as a reference point for the transformation of the transient V_{OC} to the transient n_{OC} values.[11, 22] Finally, it is possible to obtain values for the different recombination

coefficients k_{bm} and k_t (bm: bimolecular; t: trap-assisted) by fitting the relevant parts of the measured charge carrier lifetime τ (i.e. at high levels of excitation). All studied devices exhibit some bimolecular and trap-assisted recombination, which is evidenced by the respective recombination coefficients (Table 2).[22] In general, PTB7-Th:COTIC-4F and PBDBT:COTIC-4F devices exhibit the highest bimolecular recombination coefficients ($k_{bm} \approx 2.0 \cdot 10^{-11}$ cm^3/s), while PTB7-Th:CETIC-4F and PBDBT:CETIC-4F devices show values in a smaller range ($k_{bm} \approx (0.6 - 1.4) \cdot 10^{-11}$ cm^3/s). The magnitude of k_{bm} is inversely proportional to the bandgap of the studied blend system, which correlates with the results obtained *via* capacitance spectroscopy and is in agreement with what would be expected from the fundamental relationships governing bimolecular recombination.[41] In the case of trap-assisted recombination, PBDBT:CETIC-4F and PBDBT:COTIC-4F devices show nearly two orders of magnitude higher values for the relevant recombination coefficient ($k_t \approx 10^5$ s^{-1}), than the respective PTB7-Th:NFA OSCs ($k_t \approx 10^3$ s^{-1}).

Table 2. Recombination dynamics of OSCs with blends consisting of PBDBT or PTB7-Th as donor and CETIC-4F and COTIC-4F as acceptor.

Donor	NFA	FF	PCE_{max} [%]	θ_{SC}	θ_{MP}	$t_{½}$ [ms]	β_{max}	k_{bm} [cm^3/s]	k_t [s^{-1}]
PBDBT	CETIC-4F	0.54	6.59	0.1060	0.4997	0.13	1.4	$(0.60 \pm 0.02) \cdot 10^{-11}$	$(9.92 \pm 0.12) \cdot 10^4$
	COTIC-4F	0.49	2.32	0.1226	0.6544	0.06	1.4	$(2.15 \pm 0.05) \cdot 10^{-11}$	$(9.83 \pm 0.19) \cdot 10^4$
PTB7-Th	CETIC-4F	0.61	8.08	0.0241	0.2778	1.20	1.6	$(1.35 \pm 0.02) \cdot 10^{-11}$	$(1.66 \pm 0.07) \cdot 10^3$
	COTIC-4F	0.59	7.04	0.0444	0.4552	0.60	1.7	$(2.06 \pm 0.09) \cdot 10^{-11}$	$(1.54 \pm 0.16) \cdot 10^3$

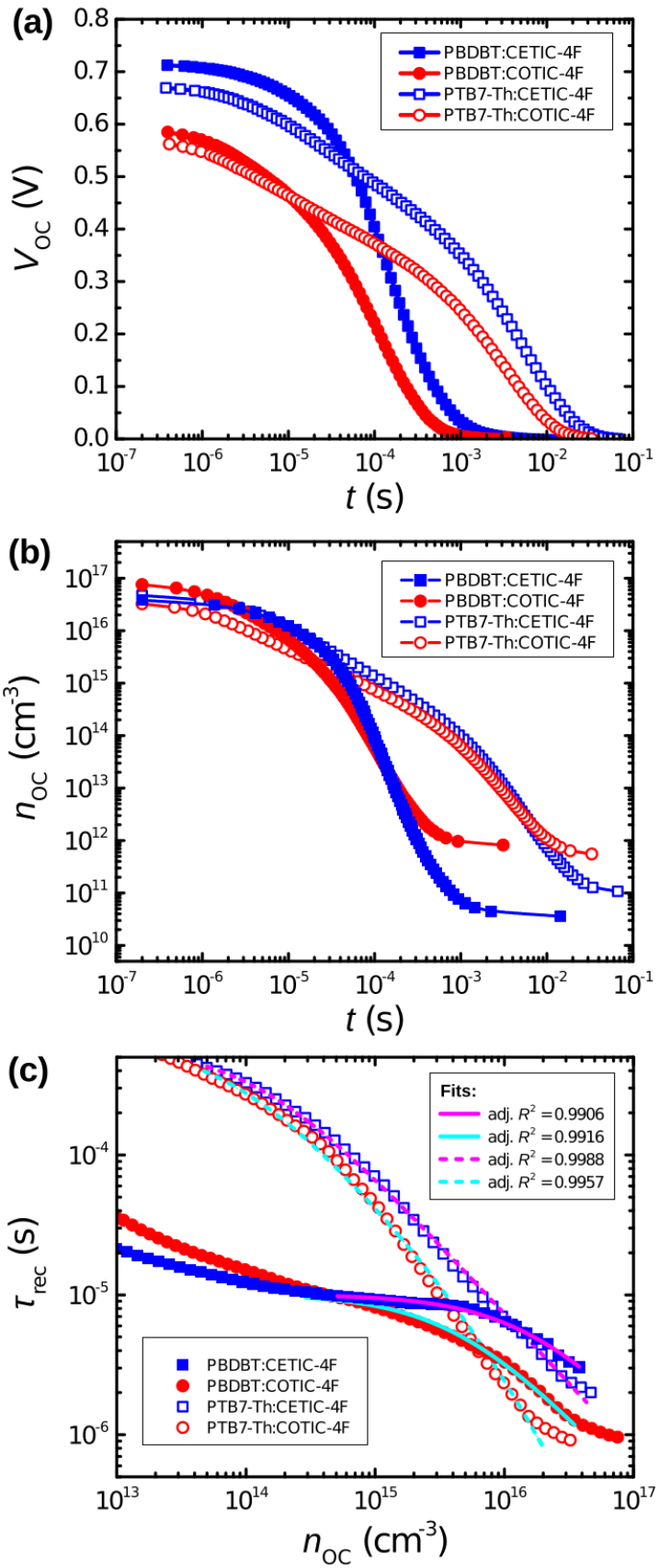

Figure 4. (a) Transients of open-circuit voltage V_{OC} and (b) open-circuit carrier density n_{OC} of the studied solar cells. (c) Charge carrier lifetime τ_{rec} vs. the transient open-circuit carrier density n_{OC} and their corresponding fits determined *via* open-circuit voltage decay.

The investigation of the morphology suggests that the order in the blend films could be responsible for the differences in trap-assisted recombination and ultimately performance that were observed for devices with the two studied donor materials. In particular, the PBDBT:CETIC-4F and PBDBT:COTIC-4F blends show less order in comparison to the PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F blends, as evidenced by GIWAXS and AFM measurements (Figures S17 and S18). The roughness in the AFM measurements is consistently higher for PBDBT:CETIC-4F and PBDBT:COTIC-4F blends than for the PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F blends. GIWAXS measurements show that there are diffraction peaks from the donor and the acceptor component in the PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F blends, while the scattering from PBDBT:CETIC-4F and PBDBT:COTIC-4F blends is dominated by the polymer. The difference in film composition (60% NFA in PTB7-Th blends and 50% NFA in PBDBT blends) is not likely to account for such a dramatic difference. This suggests that the NFA domain is significantly less ordered in blends with PBDBT than with PTB7-Th.

Our results show that the difference in trap-assisted recombination is related to whether PTB7-Th or PBDBT is being used as the donor component of the blend, whereas the difference in bimolecular recombination is related to the magnitude of the bandgap.

3. Conclusion

In conclusion, the synthesis and characterization of the new NFA CETIC-4F is described and it was shown that altering the sub-donor (D') fragments is a viable strategy to finely tune the energy levels. The performance of solar cells based on the common polymer donors PTB7-Th and PBDBT, as well as the systematically structurally modified NFAs CETIC-4F and COTIC-4F are investigated. The solar cells exhibited charge generation at wide spectral ranges (300 – 950 nm), reaching wavelengths as long as 1100 nm in the case of PBDBT:COTIC-4F and PTB7-Th:COTIC-4F. The PCEs achieved for PTB7-Th:CETIC-4F and PTB7-Th:COTIC-4F devices (8 %, and 7 %, respectively) were consistently higher than for devices employing

PBDBT:CETIC-4F and PBDBT:COTIC-4F (6 %, and 2 %, respectively). This observation could be linked to considerably higher monomolecular, i.e., bulk trap-assisted recombination losses for the PBDBT:CETIC-4F and PBDBT:COTIC-4F devices that were determined *via* analyses based on capacitance spectroscopy and open-circuit voltage decay measurements. AFM and GIWAXS results indicate that the PBDBT:NFA blend films show higher roughness and less order in contrast to the PTB7-Th:NFA blends, which likely cause the increased trap-assisted recombination. Furthermore, PTB7-Th:COTIC-4F and PBDBT:COTIC-4F devices exhibited higher bimolecular recombination coefficients than their PTB7-Th:CETIC-4F and PBDBT:CETIC-4F counterparts, which is in agreement with what would be expected from the fundamental, inverse relationship between the bandgap and bimolecular recombination.

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Supporting Information Available: Additional details about the synthesis, characterization, device fabrication, experimental setups, recombination analysis, and morphological measurements are provided in the Supporting Information.

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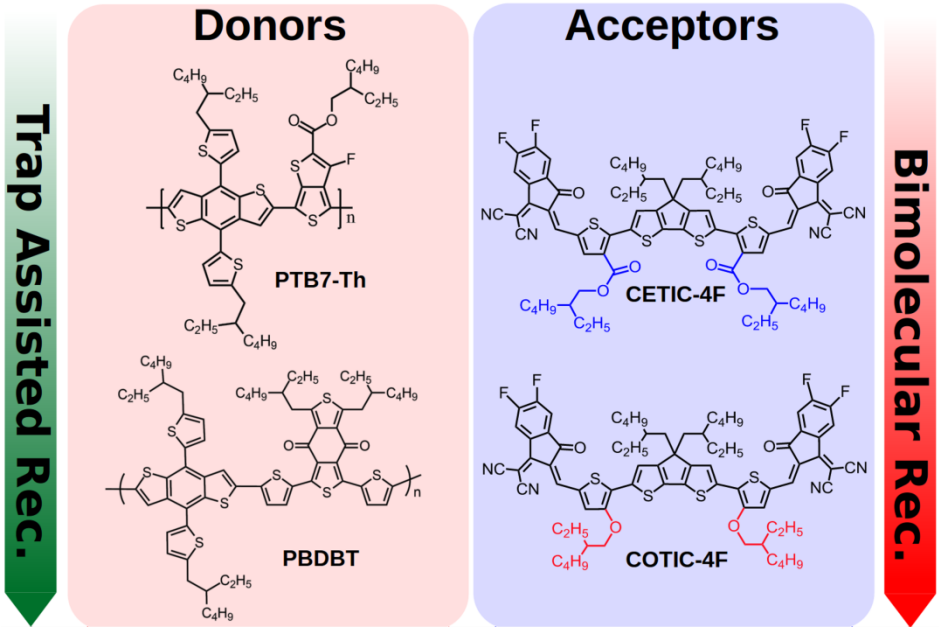
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