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The Finale of a Trilogy: Comparing Terpolymer and Ternary Blend with Structurally Similar Backbones for Organic Bulk Heterojunction Solar Cells

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Abstract:

Building on our previous works comparing the efficacy of terpolymers vs. ternary blends in improving the performance of bulk heterojunction organic solar cells, the final piece of this series of studies is focused on comparing terpolymer and ternary blends constructed with two polymers with structurally similar backbones (monoCNTAZ and FTAZ) yet with markedly different open circuit voltages (V_{oc}s). Terpolymers and ternary blends at five ratios were studied, and it is demonstrated that while the overall performance of both systems is similar, the ternary blends exhibit higher short circuit current (J_{sc}), while the terpolymers exhibit higher V_{oc}. Investigation of the charge transfer state using low-energy EQE indicates that the ternary blends are governed by a parallel-like mechanism, while the terpolymer does not follow this mechanism. The key morphological difference between the systems, as illuminated by resonance soft X-ray scattering (RSoXS), is slightly smaller (~60 nm) domains in the ternary blend compared to the terpolymer (~80 nm), which may affect exciton harvesting in the terpolymer system and lead to lower J_{sc}. In addition, a lower driving force for the charge transfer (CT) state formation likely also contributes to the lower J_{sc} in the terpolymer system. All together, these data show that structurally similar (perhaps even miscible) polymers still exhibit key differences in performance when paired in terpolymers vs. ternary blends and allow us to further illuminate the underlying mechanisms of such complex systems.

1. Introduction

While organic solar cells (OSCs) offer exciting developments for photovoltaic technology with their versatility and inexpensive fabrication, they continue to be hampered by the inherently narrow absorption window of conjugated polymers.[1] Two different strategies have thus been used to incorporate multiple conjugated polymers (ideally with complementary absorption) into the bulk heterojunction (BHJ) layer to extend the absorption range of OSCs. One strategy is the ternary blend where two donor polymers and one acceptor molecule are physically mixed, and the other one is the terpolymer where three (or more) different structural units from two parent conjugated polymers are copolymerized together (i.e., chemically mixed). Both strategies have proven to be effective methods of extending the absorbance of an organic solar cell and improving performance.[1–9] Recent efforts utilizing these strategies have yielded some of the highest efficiencies for organic solar cells (OSCs).[3,10] In fact, one of the highest reported efficiency (14.1%) of single junction OSCs was achieved with a ternary blend that included a polymer (PTB7-Th), a fullerene acceptor ($PC_{71}BM$) and a non-fullerene acceptor (CO_i8DFIC).[11] However, the success of ternary blends and even terpolymer based solar cells is still at times a largely empirical process. Several recent studies have highlighted the importance of polymer compatibility and miscibility for working ternary blend OSCs;[12–14] but given the complexity of these systems, further investigation is required.

In our own studies, we have introduced two systems where we directly compare a terpolymer with a ternary blend of its parent polymers;[15,16] such practices have allowed us to better understand the fundamental mechanisms in both systems. Initially, we investigated the terpolymer of PBnDT-DTBT (abbreviated as DTBT) and PBnDT-HTAZ (i.e., HTAZ), two parent polymers which share the same donor moiety BnDT and also showed improved performance over their binary blends when used in a ternary blend.[17,18,15] In this first system, there was a marked difference in the performance in OSCs between the terpolymer and the ternary blend: the terpolymer showed improved open circuit voltage (V_{oc}) but lower short circuit current (J_{sc}) compared to the ternary blend, possibly because the difference in the acceptor moiety (i.e., DTBT unit vs. HTAZ unit) could lead to immiscibility of these two parent polymers (DTBT and HTAZ). These observations suggested that there can be stark differences between a terpolymer and ternary blend.

In a second study, we focused on a system with similar backbones by comparing PBnDT-HTAZ (i.e., HTAZ) and PBnDT-FTAZ (i.e., FTAZ).[16] We had previously demonstrated that random copolymers of these two parent polymers (which differ solely by the addition of two fluorine atoms) displayed photovoltaic properties between those of the parent polymers.[19] In this follow-up study, we directly compared the 1:1 physical blend of HTAZ and FTAZ to the terpolymer (also 1:1 feed ratio), and a newly synthesized monofluorinated copolymer PBnDT-monoFTAZ (monoF). Surprisingly, in this system, there was no observable difference in device characteristics between the terpolymer (1:1 feed ratio) and the ternary blend (1:1 physical blend). This is a direct contrast to our previous study and serves to highlight the diversity of photovoltaic behavior in ternary blends. More importantly, this second study suggested a plausible guideline: *If the polymers are similar/miscible, they are more likely to have similar behavior in the ternary* *blend and the terpolymer*. Indeed, there have already been several examples demonstrating that the compatibility of the polymers is key to successful ternary blends.[6,12,14,20,21]

Building on these studies, we have moved on to what may prove to be an ideal terpolymer/ternary blend system by selecting PBnDT-monoCNTAZ and PBnDT-FTAZ (abbreviated as monoCNTAZ and FTAZ in **Figure 1**) as our parent polymers. Unlike DTBT and HTAZ, these two polymers share a structurally similar acceptor moiety (benzotriazole, TAZ), in addition to sharing the same donor moiety BnDT. Thus, these two polymers would likely be 'miscible', from a structural point of view. However, the switch from a fluorine substituent to the stronger electron withdrawing cyano group results a smaller band gap of monoCNTAZ (1.85 eV).[22] Thus this system is an improvement on the HTAZ:FTAZ system where these two polymers show almost identical absorption, since the current system (monoCNTAZ and FTAZ) has the potential for increased J_{sc} from extended absorbance, a key motivator behind both ternary blends and terpolymers.[7,23] Furthermore, the highest occupied molecular orbital (HOMO) level of monoCNTAZ is slightly deeper than that of FTAZ (– 5.58 eV vs. – 5.45 eV), which leads to a higher V_{oc} for monoCNTAZ based devices than that of FTAZ based ones (0.935 V vs. 0.811 V, *vide infra*, **Table 1**).

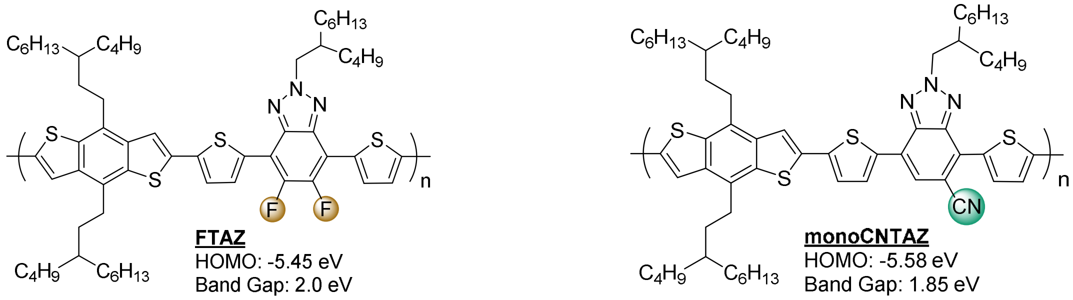


Figure 1. The structures, HOMO energy levels, and bandgaps for the two parent polymers used in this study.

With the interesting features of this new system, we designed our study to compare the terpolymer of these two parent polymers to the ternary blend at five monoCNTAZ:FTAZ (mC:F) ratios (9:1, 7:3, 1:1, 3:7 and 1:9), to further explore the differences between terpolymer and ternary blend. Should the polymers show compatible *and* cooperative behavior, there may be a corresponding overall increase in the photovoltaic performance of the ternary blends due to improved morphology, as has been demonstrated in the literature.[24–27] Furthermore, the significant difference in V_{oc} between these parent polymers based bulk heterojunction (BHJ) solar cells provides an ideal pairing to study the effect of terpolymer vs. ternary blend on V_{oc}, an often debated subject in ternary blend OSCs, especially since the terpolymer mimics the close intermixing required for the suggested alloy model.[12,28]

Not surprisingly, we found that, upon physically blending monoCNTAZ and FTAZ (i.e., the ternary blend), the V_{oc} of the ternary blend OSCs is composition dependent, which is the hallmark of a working parallel-like or alloy model bulk heterojunction.[2] However, the overall performance is the average of both parent polymers, and there is no *enhanced* efficiency (which is only possible if the polymers are compatible *AND* behave cooperatively). When directly comparing the performance of the terpolymer and the ternary blend OSCs at each monoCNTAZ:FTAZ (mC:F) ratio, the overall performance is interestingly very similar, but there are marked differences in the V_{oc} and J_{sc}. On the other hand, the fill factor (*FF*) is maintained for both the terpolymer and the ternary blend OSCs. With a more significant change to the backbone (i.e., fluorine to cyano) than in our previous study (i.e., hydrogen to fluorine in the case of HTAZ and FTAZ), despite the compatibility of these polymers, there is a marked difference between the terpolymer and the ternary blend. These results highlight the complexity of such systems, but also demonstrate that high performance ternary blends are within reach as we unravel more the underlying operating principles.

2. Experimental

All chemicals were purchased from commercial source (Sigma-Aldrich, Fisher, Matrix, etc.) and were used as received except when specified. Tris(dibenzylideneacetone) -dipalladium(0)-chloroform adduct (Pd2dba3·CHCl3) was purchased from Sigma-Aldrich and was recrystallized in chloroform/acetone. Tri(o-tolyl)phosphine (P(o-tol)3) was recrystallized in hexanes.

Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 220 instrument, using 1,2,4-trichlorobenzene (TCB) as the eluent (stabilized with 125 ppm BHT) at150 °C. Further details regarding the synthesis of the polymers (including GPC and elemental analysis) can be found in the SI.

UV-Vis spectra were measured on glass for the neat polymer films, or on ITO/CuSCN for the devices using a Shimadzu UV-2600 spectrophotometer.

Cyclic Voltammetry (CV)

CV measurements were carried out on solid films using a Bioanalytical Systems (BAS) Epsilon potentiostat with a standard three-electrode configuration. A three electrode cell of a glassy carbon working electrode, $Ag/AgNO_3$ reference electrode and Pt counter electrode were used. Films were drop-cast onto the glassy carbon electrode from hot chloroform solution (2 mg/mL, with tetrabutylammonium hexafluorophosphate added at 100% wt% relative to polymers) and dried using a heat gun. 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as a supporting electrolyte. Scans were carried out under argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple. The HOMO in electron volts was calculated from the onset of the oxidation potential (E_{ox}) according to the following equation:

$$HOMO = -[4.8e + e(E_{ox} - E_{Fc/Fc^+})]$$

Photovoltaic Device Fabrication

Device fabrication began with cleaning indium tin oxide subtrates by sonicating in deionzied water, acetone, and isopropyl alcohol, then subjecting them to UV-Ozone treatement for fifteen minutes. CuSCN dissolved in diethylsulfide was spuncast at 7000 rpm to create a 50 nm film and annealed at 100 ºC for 10 minutes. All subsequent steps were carried out under nitrogen atmosphere. The active layer was spuncast from solutions of polymer(s):$PC_{61}BM$ (1:2) in trichlorobenzene, which were heated for 6 hours at 130 ºC. Such conditions are necessary to fully dissolve the monoCNTAZ, which is prone to aggregation and can be difficult to work with at the concentrations necessary for spincasting. The $PC_{61}BM$ was purchased from Nano-C and used as received. The active layer was then deposited (while still hot) through a 1 um poly(tetrafluoroethylene) filter and spun to achieve the desired film thickness. Films were immediately dried under vacuum for twenty minutes. As a top electrode, 30 nm of calcium was deposited via thermal evaporation, followed by 70 nm of aluminum, both at 3×10^{-6} mbar. All photovoltaic devices were measured under AM 1.5G irradiation (100 mW/cm^2, Oriel 91160, 300 W) calibrated using an NREL certified standard silicon cell, and recorded using a Keithley 2400 digital source meter. Reported values are the average of at least 6 devices (active area 13 mm^2) with standard deviation. Thickness of the active layer was measured by an Alpha Step D-100 KLA -Tencor profilometer.

Space Charge Limited Current (SCLC)

To measure the hole mobilities, devices with the structure ITO/CuSCN/ActiveLayer/MoO3 (10nm)/ Al (70nm) were fabricated. The active layer was fabricated under the same conditions used for the photovoltaic devices. Current was measured as a function of voltage in the dark from -1 to 5 V using a Keithley 2400 digital source meter. Mobilities were calculated according to the Mott-Gurney Law:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\frac{V^2}{d^3}\mu$$

where ε_r is the dielectric constant of the organic semi-conducting materialmaterial (estimated to be about 3), ε_0 is the permittivity of free space, d is the thickness of the film. To calculate the mobility, a fit was applied to the $J^{0.5}$ vs. V curve in the SCLC regime.

Energy of the CT State

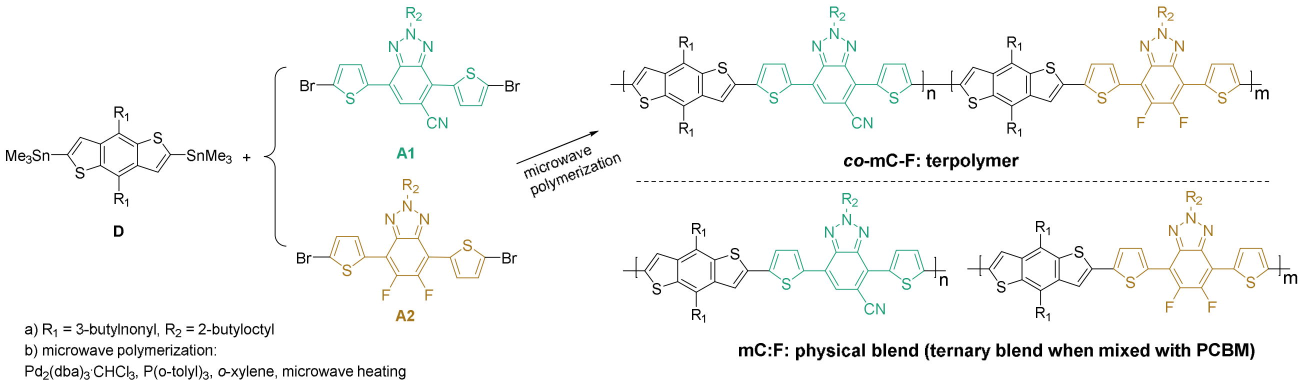
The CT state was estimated as previously described by fitting the equation below to a normalized EQE spectra.[29]

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

3. Results and Discussion

3.1 Synthesis

The terpolymers of these two parent polymers were synthesized at various mC:F ratios by controlling the feed ratio of the cyanobenzotriazole monomer, the difluorobenzotriazole monomer, and the benzodithienyl monomer (**Scheme 1**), as was previously reported for the HTAZ:FTAZ system.[15,19] The incorporation of the cyano and fluorine groups was verified via elemental analysis (see Supplemental Information). It should be noted that due to the random nature of the polymerization, there may be some irregularities along the backbone, including "oligomeric sections" where several BnDT-FTAZ units repeat in a row. In our previous study, such random terpolymers outperformed their regular counterparts, so the synthetically difficult, regular terpolymer is not investigated here.[15] For clarity, the terpolymers will be referenced using "*co*-mC-F 1:9" (i.e., copolymer that has a feed ratio of A1 vs. A2 = 1:9 in **Scheme 1**), for example, and the ternary blends will simply be "mC:F 1:9" (i.e., blending ratio of monoCTAZ vs FTAZ = 1:9, wt%).



Scheme 1. Synthesis of terpolymers, compared with the ternary blend

Cyclic voltammetry was measured for each of the resulting polymers. The terpolymers with greater than 10% CNTAZ unit, had similar HOMO levels to the monoCNTAZ polymer. These values are tabulated in Table S3 in the SI.

3.2 UV-Vis Absorbance

We first investigated the effect of blending monoCNTAZ and FTAZ (i.e., terpolymer or ternary blend) on the absorbance of these polymers based BHJ blend (polymer:$PC_{61}BM$ = 1:2, **Figure 2**). In addition, the calculated absorbance coefficients for each ratio (i.e., the weighted average of the FTAZ and monoCNTAZ absorbance) are included for a theoretical comparison.

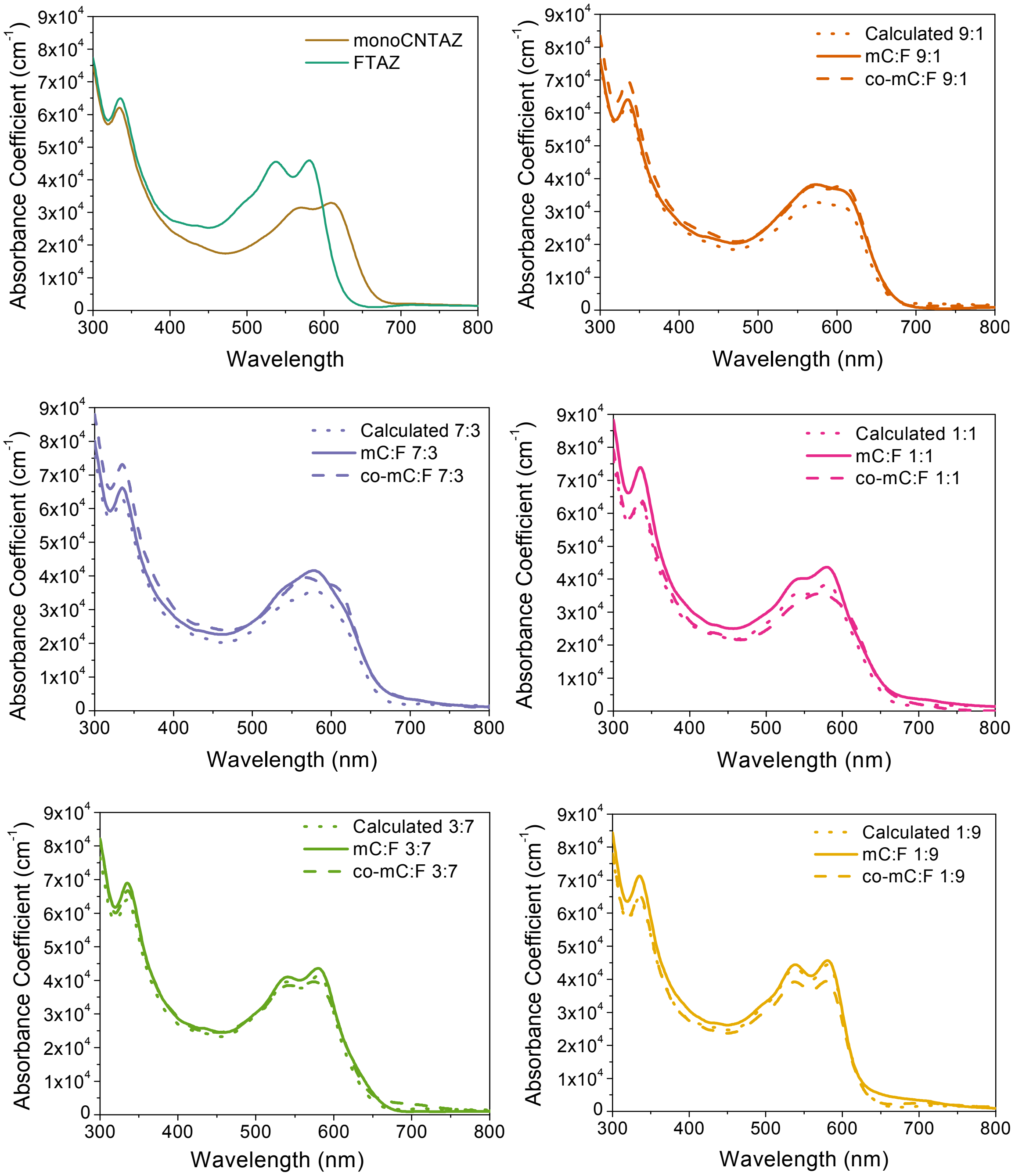


Figure 2. Absorbance spectra of BHJ blends (polymer:$PC_{61}BM$ =1:2, weight ratio) for the parent polymers, and all other terpolymers and ternary blends of monoCNTAZ and FTAZ. The solid lines

indicate the ternary blends, dashed lines are the terpolymer, and the dotted lines are the calculated expected absorbance.

In four of the five ratios (the mC:F 1:9, 3:7, 7:3 and 9:1), the terpolymers and ternary blends show almost identical absorbance peaks, and these agree well with the theoretical calculation based on the weighted absorbance of FTAZ and monoCNTAZ. This observation indicates that the absorbance of the terpolymers and ternary blends is essentially the weighted average of the absorbance of the parent polymers. This would suggest that for most of these blends, there are no significant differences in the absorption (between the terpolymers and ternary blends) which would lead to a change in the photovoltaic behavior. However, the *co*-mC-F 1:1 terpolymer shows markedly less aggregation from 500 – 600 nm than the 1:1 ternary blend. This is a departure from the other ratios, but has been observed in the previously studied DTBT: HTAZ system, where it was suggested that the observed difference in aggregation could lead to low local mobility and lower performance.[15] In the ternary blend, the polymers can aggregate separately without interfering with each other; however, in the terpolymer, the random nature of the polymerization increases irregularities along the backbone and decreases aggregation. Nevertheless, given the overall similarities, it is unlikely that absorbance would lead to any difference in the device performance of these systems.

3.3 Photovoltaic Performance

We next investigated the device performance of all materials in this work. Devices were fabricated in the following conventional structure: ITO/CuSCN/BHJ/Ca/Al. Thicknesses of the BHJ layer were maintained at approximately 200 nm to limit the effects of thickness on the device performance. The performance for all devices is included in **Table 1**, with individual device parameters are compared in **Figure 3**.

Table 1. The photovoltaic performance of all of the systems investigated in this study.

Polymer	**Thickness**	**Jsc**	**Voc**	**FF**	**PCE**
monoCNTAZ	202 ±1	13.30 ±0.43	0.935 ±0.001	68.9 ±2.0	8.57 ±0.34
mC:F 9:1	202 ±1	13.44 ±0.2	0.920 ±0.002	66.9 ±1.4	8.25 ±0.21
mC:F 7:3	213 ±5	13.23 ±0.26	0.883 ±0.003	65.9 ±2.2	7.70 ±0.33
mC:F 1:1	202 ±15	12.95 ±0.14	0.867 ±0.003	68.2 ±2.4	7.66 ±0.33
mC:F 3:7	218 ±13	12.71 ±0.37	0.850 ±0.003	68.7 ±1.1	7.42 ±0.21
mC:F 1:9	202 ±46	11.80 ±0.12	0.828 ±0.002	72.1 ±1.3	7.05 ±0.13
FTAZ	217 ±14	11.76 ±0.31	0.811 ±0.004	70.7 ±1.5	6.74 ±0.26
***co*-mC-F 9:1**	224 ±32	12.62 ±0.57	0.922 ±0.003	68.1 ±2.1	7.92 ±0.49
***co*-mC-F 7:3**	209 ±8	12.36 ±0.43	0.904 ±0.003	69.5 ±2.0	7.77 ±0.31
***co*-mC-F 1:1**	227 ±5	12.37 ±0.32	0.899 ±0.001	66.7 ±2.8	7.42 ±0.37
***co*-mC-F 3:7**	240 ±11	11.98 ±0.31	0.863 ±0.002	68.7 ±3.9	7.11 ±0.5
***co*-mC-F 1:9**	244 ±20	11.57 ±0.38	0.834 ±0.001	68.5 ±3.0	6.61 ±0.37

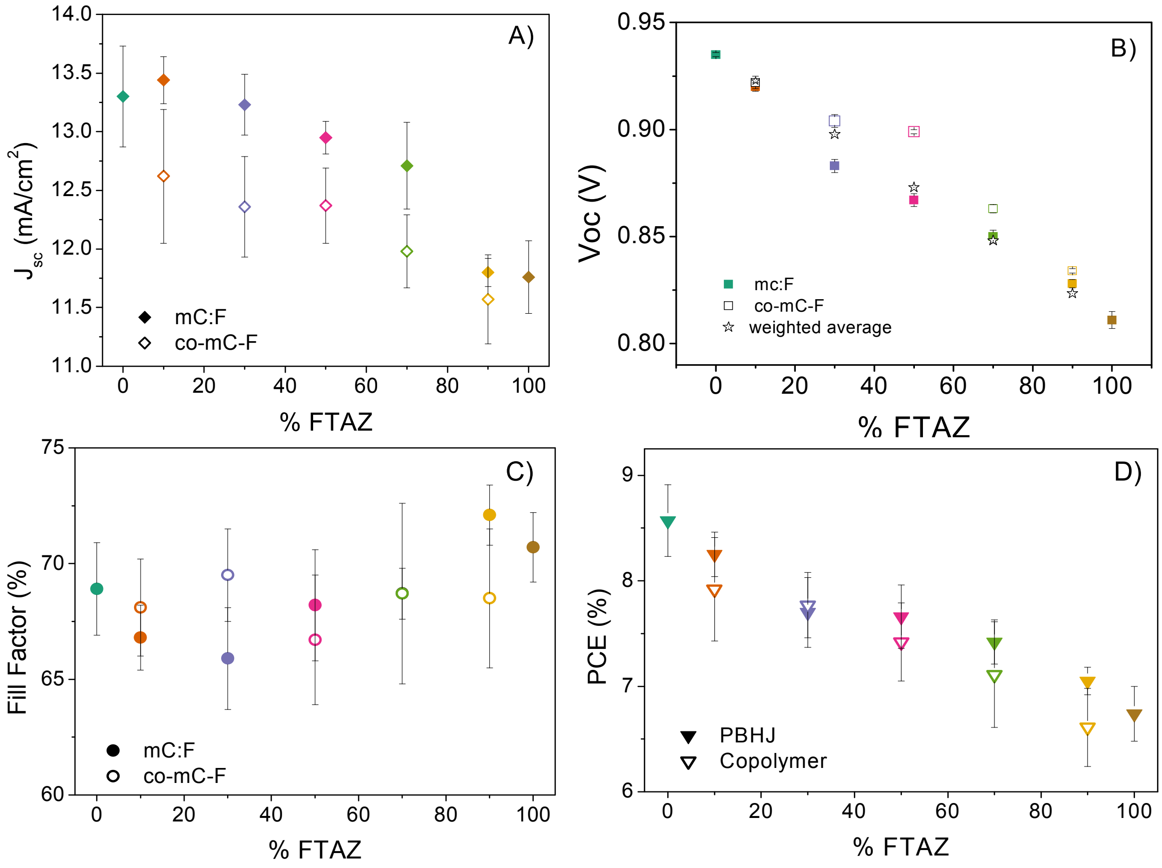


Figure 3. The photovoltaic device performance for the systems studied. Open symbols indicate the terpolymer, while closed symbols are the ternary blend and binary parent blends.

<u>Short Circuit Current Density:</u> First, the short circuit current density (J_{sc}) of the ternary blends and terpolymers based BHJ devices both trend with composition, increasing as the amount of monoCNTAZ is increased (**Figure 3a**). For the mC:F 9:1 and 7:3 ternary blends, the J_{sc} is maintained at that of monoCNTAZ, but as more FTAZ is added (from mC:F 1:1 on), the J_{sc} continues to drop until at the 1:9 ratio, where it is essentially equal to that of FTAZ based devices. This is not unexpected, since monoCNTAZ offers noticeably higher J_{sc} than FTAZ and its absorption spectrum significantly overlaps with that of FTAZ. Replacing the better light-to-current converter (i.e., monoCNTAZ) with the lesser one (i.e., FTAZ) would thereby lead to a lower J_{sc} of the ternary blend. Interestingly, when we compare the terpolymers to the ternary blends, the terpolymers have a lower J_{sc} across all mC:F ratios (**Figure 3a**). Given the equivalent absorbance spectra between the terpolymer and ternary blends (except for the 1:1 ratio), this difference of J_{sc} would not stem from a difference in absorbance. Furthermore, as will be discussed below, the fill factor is maintained at all ratios and not statistically different between terpolymer and ternary blends, which may suggest similar charge extraction behavior.[16] Therefore, another explanation for this stark difference in J_{sc} is required, and will be posited below. Nevertheless, the difference in J_{sc} between the terpolymer and the ternary blend at each ratio is not significant (<10%).

Open Circuit Voltage: Both the ternary blends and the terpolymers exhibit the composition dependent V_{oc}, which is a key hallmark of the parallel-like bulk heterojunction (PBHJ) or the alloy charge generation mechanism (**Figure 3b**).[2,30–32] This observation indicates that both polymers are participating in charge transport, as the V_{oc} would be pinned if all charges were transported through one polymer. For the ternary blends, the V_{oc} has a linear dependence on ratio, and *agrees with the weighted average of the V_{oc} values of these two binary blends*. This offers strong evidence that the ternary blend in this study follows the PBHJ model.[4] However, for the terpolymers at either 7:3, 1:1 or 3:7 ratio, the value of V_{oc} is significantly higher than that of the corresponding ternary blend. Since our terpolymers mimic the close intermixing of the components that would be required for an alloy model,[28,30,33] the observed different values of V_{oc} for the ternary blend and the terpolymer with the identical ratio (i.e., 7:3, 1:1 or 3:7) imply that the alloy model does not apply in the current system. This is in direct contrast to the previously studied HTAZ: FTAZ system where the values of V_{oc} of the terpolymer and ternary blend were essentially identical, but has been observed in the previously discussed DTBT:HTAZ system.[15] This intriguing behavior was further investigated by directly measuring the energy of the charge-transfer state, as will be discussed below.

Fill Factor: Since both polymers have a relatively high *FF* to start (above 65%), the fill factor is maintained in both the terpolymers and the ternary blends (**Figure 3c**). While this was somewhat expected, it is noteworthy, since the difference in backbone between FTAZ and monoCNTAZ could have significantly disrupted the morphology, with a corresponding drop in *FF*. However, there appears no beneficial cooperation in these ternary blends that would lead to higher *FF*; yet such increased *FF* has been seen in other ternary blends.[34–37]

Power Conversion Efficiency: Since the J_{sc} and V_{oc} behavior are both composition dependent, and *FF* is maintained, the overall power conversion efficiency (PCE) for both the terpolymers and ternary blends is also composition dependent (**Figure 3d**). However, while the efficiency values for the terpolymer and ternary blends are similar, this behavior is not equivalent since it stems from the difference in V_{oc} behavior and J_{sc} behavior essentially cancelling each other out. This is different than the HTAZ:FTAZ system, which had equivalent PCE for the terpolymer and ternary blend *because of* equivalent V_{oc} and J_{sc} (and *FF*).[16] On the other hand, the DTBT:HTAZ system has different behavior in PCE *and* individual device characteristics (V_{oc}, J_{sc} and *FF*) for the terpolymer and the ternary blend;[15] specifically, the increase in V_{oc} for the terpolymer could not make up for the decrease in J_{sc}, resulting in an overall lower performance of the terpolymer. These differences in terpolymer vs. ternary blend behavior highlight the important nuances of these complex systems. Despite the fact that ultimately both the terpolymer and ternary blends achieved the same PCE in this study, the monoCNTAZ:FTAZ system behaves very differently than our previously studied two systems.

External Quantum Efficiency: While the composition dependent V_{oc} indicates that both polymers would be contributing to the PCE, the external quantum efficiency (EQE) was measured to confirm this. **Figure 4** includes the parent polymer EQEs and the 1:1 ratio terpolymer and ternary blend (additional EQE are shown in the SI, ***Figure S3***). Notably, both polymers are seen to contribute in the 1:1 ratio for both the terpolymer and the ternary blend, with clear contribution from monoCNTAZ in the 650-700 nm range and from FTAZ in the 450-500 nm range. The peak at 700 nm is from PCBM, and has been previously documented.[18]

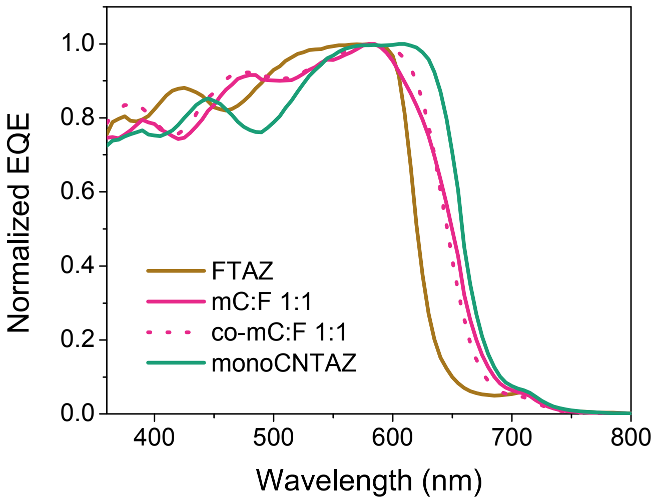


Figure 4. EQE of the parent binary blends, the 1:1 ratio terpolymer, and 1:1 ternary blend.

3.4 Comparison of V_{oc} and E_{CT}

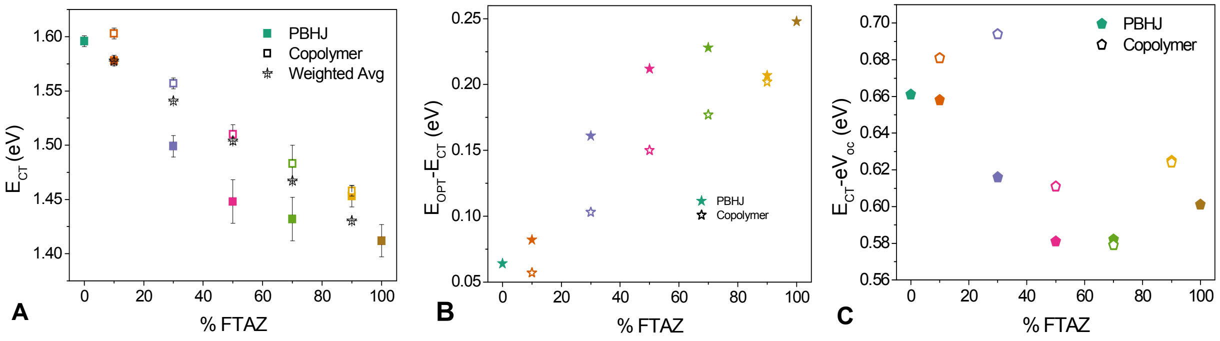


Figure 5. a) Energy of the CT state as calculated from low-energy EQE, stars represent the weighted average of the CT energies from the parent binary blends, b) energy difference between the optical bandgap of $PC_{61}BM$ (the smallest in the system) and the energy of the CT state, and c) the energy difference between the energy of the CT state and the observed V_{oc}.

In recent years, the importance of the charge transfer (CT) state has come to the forefront of the discussion surrounding OSCs, as the energy of the CT state (E_{CT}) has a direct effect on the effectiveness of charge transfer within the solar cell and has a strong influence on the V_{oc}.[30,38,39] More importantly, it has been a key component in understanding the working mechanism of ternary blends.[32] Experimentally, we used sensitive, low-energy EQE measurements to directly excite and collect charges from the CT state, as has been previously described in the literature.[38,40] These EQE were fitted and E_{CT} was extracted (method described in the SI) which are shown in **Figure 5**.

As discussed earlier, the linear dependence of V_{oc} on the composition (**Figure 3b**) indicates that the current ternary blend system likely operates with a PBHJ mechanism.[2,7] This PBHJ mechanism has also been supported by other studies.[41] Further, Savoie *et al.* applied a density weighted linear combination of the neat polymer density of states (DOS) to estimate the ternary DOS, which could account for the composition dependence of V_{oc} in the PBHJ cells.[4] More recently, Felekidis *et al.* applied a more accurate and sophisticated model to estimate the effective hole DOS at the quasi Fermi level to explain this composition dependence of V_{oc} in a number of systems.[21,31] It appears that the method proposed by Felekidis *et al.* is perhaps the more applicable model at this point, in particular, after the most recent refining of their model by factoring in the energetic disorder in the donor-acceptor mixed BHJ.[21]

On the other hand, Thompson and coworkers introduced another model, the organic alloy model, to explain the composition dependence V_{oc} in their cases.[30,33,42] They further measured the E_{CT} of a series of ternary blends and found it correlated strongly to the observed V_{oc}.[30] Subsequently, Kouijzer *et al*. modelled the E_{CT} of a series of ternary blends both using an alloy model (where it is assumed an electronic alloy of the two polymers is formed, featuring a delocalized charge transfer state) and a parallel-like bulk heterojunction model (each polymer forms its own charge transfer state and the "averaged" behavior in V_{oc} is observed).[32] Though they offered evidence on having two distinct CT states in their system, the *J*-*V* curves of the ternary blends modeled with the PBHJ could only partially explain the observed sub-linear dependence of V_{oc} on the composition of the ternary blend. When we applied the weighted linear combination of the E_{CT} to our ternary blends, a clear deviation of the experimental results from the model can be seen in **Figure 5a**. This offers evidence that the 'two CT states' model does not truly apply in the current ternary system, either.

Having obtained the E_{CT} also allows us to investigate more device related physics. For example, the difference between the lowest optical bandgap in the blend (in this case, $PC_{61}BM$) and the E_{CT} of the systems is indicative of the driving force for forming the CT state ($E_{OPT} - E_{CT}$). Interestingly, due to their higher E_{CT}, and by extension higher V_{oc}, the terpolymers have a much lower driving force for CT state formation than the ternary blends for each blending ratio (**Figure 5b**). This may be one of the contributing factors to limiting the J_{sc} in the case of terpolymers based BHJ devices, since a lower driving force might lead to slightly lower amount of the formed CT states in the terpolymer. Additionally, by calculating the difference between E_{CT} and eV_{oc}, we can assess the combined radiative and non-radiative losses in the blends. **Figure 5c** shows that there is no definitive trend for the combined losses as a function of ratio; but for the monoCN:FTAZ=9:1, 7:3, and 1:1 ratios, the terpolymers show noticeably more recombination than the comparative ternary blend, which may also contribute to the drop in J_{sc}.

3.5 Mobility

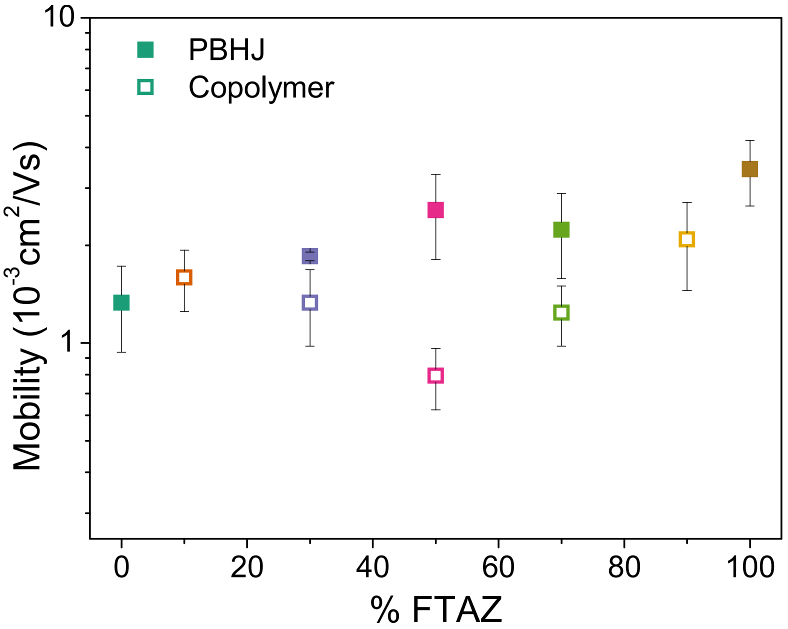


Figure 6. Hole mobility for selected blends, terpolymers, and binary parent polymers mixed with $PC_{61}BM$ and measured via the SCLC devices.

In previous systems featuring FTAZ, the physical addition of the fluorinated polymer improved the *FF* due to an improvement in hole mobility.[16,19] Here, since monoCNTAZ already exhibits a similar mobility to FTAZ, we would not expect a significant increase of the hole mobility for the ternary blends. Indeed, as shown in **Figure 6**, the hole mobility is maintained at 10^{-3} cm^2 V^{-1} s^{-1} for both the terpolymers and the ternary blends. The 1:1 terpolymer does show a significantly lower hole mobility than the 1:1 ternary blend, but this difference does not seem to have a large effect on the device performance, as their fill factors are not statistically different. This lower hole mobility of the 1:1 terpolymer may be due to the decrease in aggregation, as evidenced in the UV-Vis absorbance spectra.

3.6 Morphology

The morphology of the active layer plays an important role in the performance of the solar cell.[43] Since the performance of a binary solar cell is already dependent on the formation of meta-stable, bi-continuous donor and acceptor domains with a mixed third phase between these two, the addition of a third component further complicates the system. The comparison of the terpolymer blend film morphology to that of the ternary blend is especially interesting for our system, since one might expect the addition of a second polymer (i.e., the tertiary component) to drastically influence domain formation (unless the second polymer was miscible, as has been posited previously). In order to investigate the device morphology, we performed grazing-incidence wide-angle x-ray spectroscopy (GIWAXS), which probes the molecular morphology of the crystalline and semi-crystalline portions of the material, and resonant soft X-ray scattering (RSoXS), which probes the domain spacing and polymer:fullerene composition variations. For simplicity, we have focused on the 1:1 terpolymer and 1:1 ternary blend (both blended with $PC_{61}BM$).

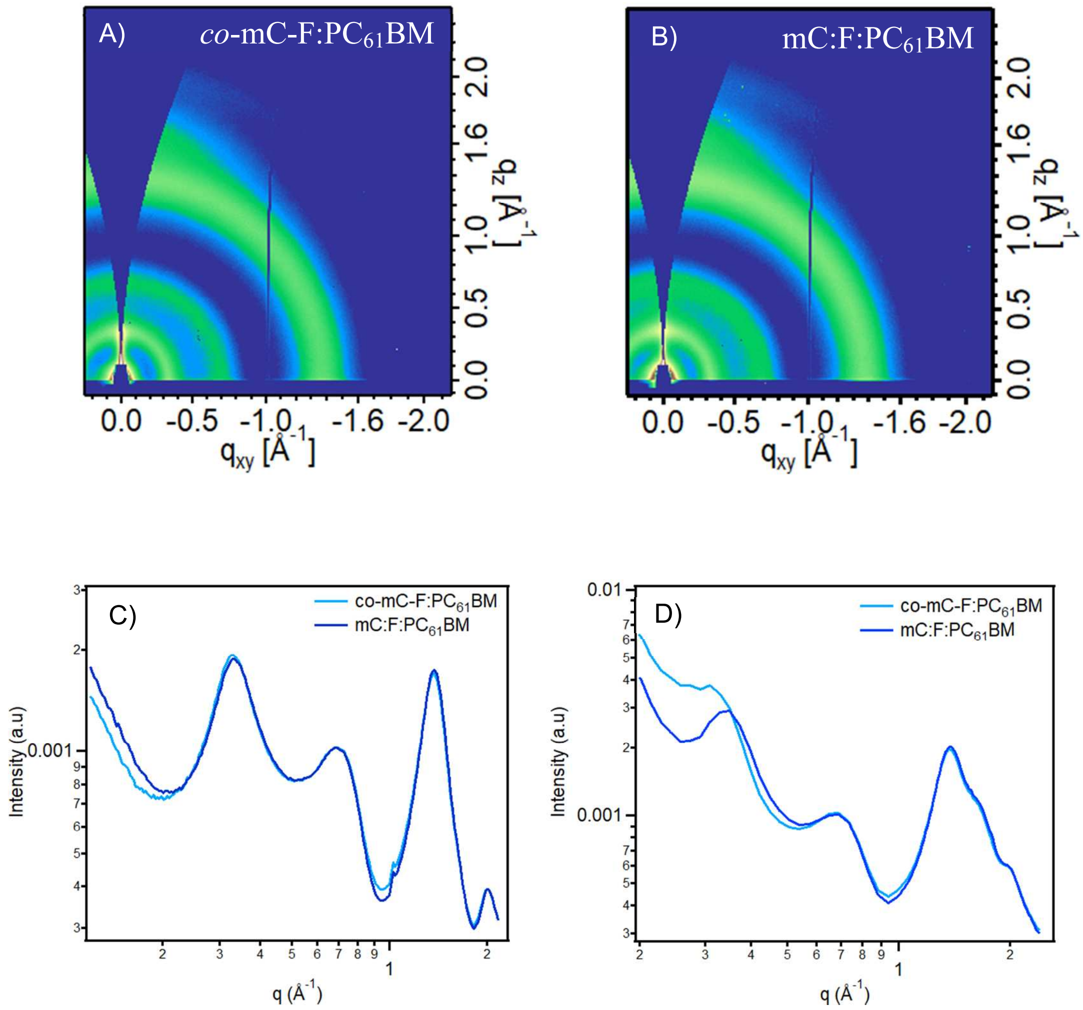


Figure 7. 2-D patterns and 1-D linecuts for the 1:1 terpolymer and ternary blend based BHJ (polymer:$PC_{61}BM$=1:2) in C) in plane and D) out-of-plane directions.

Table 2. Peak position and stacking distance as measured by GIWAXS

BHJ Blend	(010) Peak Position ($Å^{-1}$)	π- π Stacking Distance (Å)
***co*-mC-F 1:1**	1.369	4.587
mC:F 1:1	1.370	4.584

GIWAXS: The 2D patterns for both the terpolymer and the ternary blend are very similar, as are the 1D linecuts (**Figure 7**). This suggests that despite the slight difference in observed aggregation in the UV-Vis, the molecular packing of these two blends is very similar. Additionally, the pi-pi stacking distance is comparable for both films (**Table 2**). From these results, the molecular packing likely does not play a role in the differences in J_{sc} or V_{oc} for these devices.

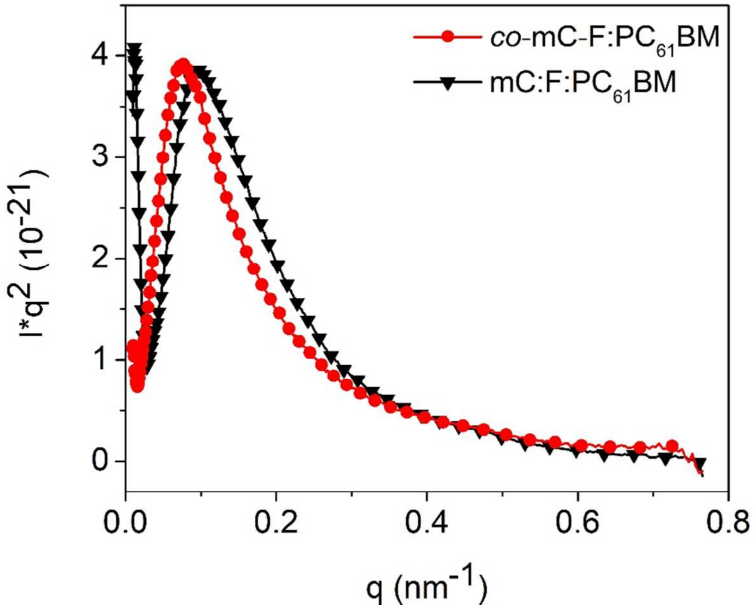


Figure 8. Lorentz corrected RSoXS (283.2eV), normalized for thickness.

Table 3. Domain spacing and purity as measured by RSoXS

Blend	Peak Position (nm^{-1})	Domain Spacing (nm)	Average Domain Purity
***co*-mC-F 1:1**	0.076	82.6	0.92
mC:F 1:1	0.100	62.8	1

RSoXS: Measuring the donor:PC$_{61}$BM domains via RSoXS unearths one of the key differences between the terpolymer and the ternary blend: the domain size. The terpolymer shows a slightly larger domain spacing than the ternary blend, with domain sizes of 82.6 nm and 62.8 nm, respectively. This increase in domain size is likely responsible for the lower J_{sc} in the terpolymer as compared to the ternary blend (in addition to the lower driving force as revealed via low-energy EQE), as the larger domains make it more difficult to effectively harvest excitons. Additionally, the ternary blend domains have slightly higher purity, which is consistent with the higher *FF* of the ternary blend (68.2%) compared to the terpolymer (66.7 %). Interestingly, despite the addition of a third component, the ternary blend is able to form slightly smaller, purer domains than the terpolymer, to the benefit of the J_{sc}. It is worth noting that additional optimization of the processing conditions may decrease the domain size, improving the terpolymer performance.

4. Conclusion

This study sought to compare a terpolymer to a ternary blend of two high performing polymers, FTAZ and monoCNTAZ, at a wide range of ratios. It is, in fact, the culmination of a series of studies on such systems. Initially our investigation of the DTBT:HTAZ ternary blend/terpolymer systems (featuring two polymers with structurally different acceptor units in the polymer backbone) led us to believe that terpolymers were an unnecessary, complex synthetic target, since, in that case, the ternary blend outperformed the terpolymer in $PC_{61}BM$ based BHJ solar cells. However, additional characterization of the HTAZ:FTAZ system (including a closer look at the charge generation and transport) showed little to no difference between the terpolymer and the ternary blend, a conclusion at odds with our previous assessment. In order to further explore this topic, we present this study, in which two high performance polymers that still share the similar backbone (i.e., PBnDT-TAZ) yet with different substituents (CN and F) are blended in a terpolymer and a ternary blend. These two parent polymers have a significant difference in V_{oc} ($\Delta\ V_{oc} \sim 0.13$ V), allowing us to investigate how V_{oc} changes with terpolymer vs. ternary blend. We were able to measure the E_{CT} of these ratios, and note that a shift in the E_{CT} can explain the higher V_{oc} of the terpolymer, a piece of data missing from the previous DTBT:HTAZ study. In turn, the lower J_{sc} of the terpolymer stemmed from a lower driving force for CT state formation and slightly larger and less pure domains in the terpolymer based BHJ blends. This system serves to highlight the complexity and diversity of such ternary systems and provides a key perspective when viewed in the context of previous studies.

Furthermore, the wide range of ratios studied make this system particularly interesting for considering the differences between the alloy and parallel-like models of charge generation and extraction for ternary blends. The ternary blends in this study show a linear dependence on the blending ratio of two parent polymers and agree with the weighted average of the V_{oc} values of the two binary blends. This observation is more in line with the PBHJ model elaborated by Saviore *et al*. and the DOS model introduced by Felekidis et.al.[32,44] Moreover, the trend of measured E_{CT} in regard to the blending ratio clearly deviates from the weighted linear combination of the E_{CT} of the two binary blends, indicating the “two CT states” model proposed by Kouijzer *et al*. does not apply to our system. Thus, the monoCNTAZ:FTAZ ternary blend seems to be governed by a parallel-like mechanism, rather than an alloy model.

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Conflicts of interest

There are no conflicts to declare

Footnotes

Supporting Information. Synthetic details, GPC curves, elemental analysis, CV scans and CT state fittings are available in the supporting information.

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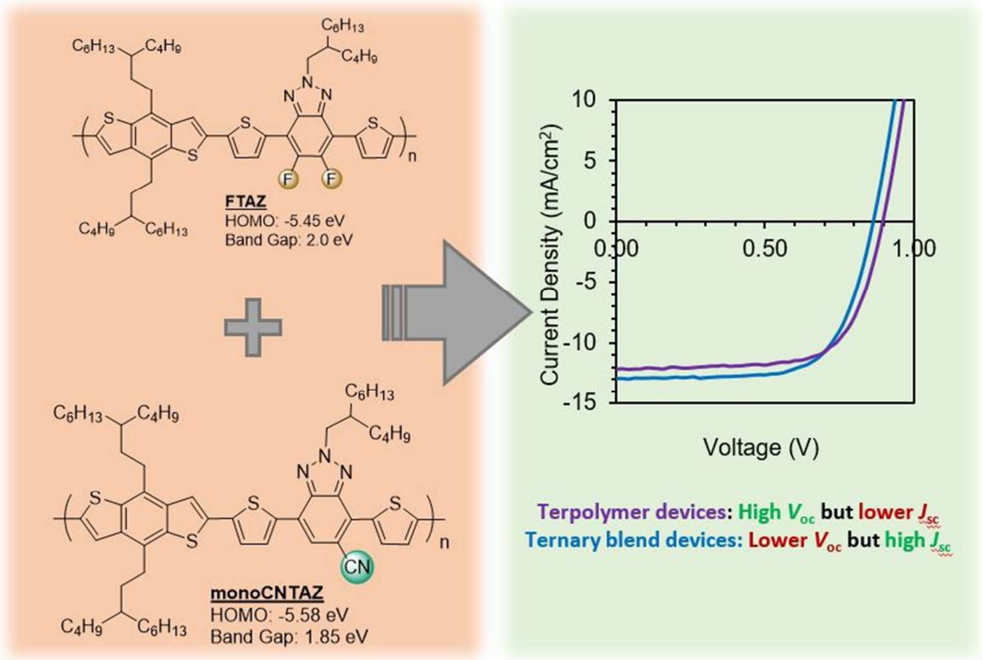

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