Ternary Blend Organic Solar Cells Incorporating Ductile Conjugated Polymers with Conjugation Break Spacers

*Negar Kazerouni, Elizabeth L. Melenbrink, Pratyusha Das and Barry C. Thompson**

Department of Chemistry and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661

ABSTRACT. A broad family of ductile semi-random donor-acceptor (D-A) copolymers with 8-carbon alkyl conjugation break spacer (CBS) units were incorporated into ternary blend organic solar cells in order to determine their impact on the electrical metrics of solar cell performance. The goal of this study was to elucidate potential co-optimization strategies for photovoltaic and mechanical properties in organic solar cells. The ternary blended active layers were based on two polymer donors and the acceptor [6,6]-Phenyl-C61-butyric acid methyl ester ($PC_{61}BM$). In all

cases, the majority polymer donor component was the previously reported fully conjugated semi-random polymer P3HTT-ehDPP-10%, comprised of 80% 3-hexylthiophene, 10% diketopyrrolopyrrole (DPP) with 2-ethylhexyl (eh) side chains, and 10% thiophene. As the second donor, three different classes of CBS polymers were used, where the spacer length was kept constant at 8 methylene units. The mechanical properties of these polymers are quite notable with moduli as low as 8.54 MPa and fracture strains as high as 432%. However, it was found that as ductility increased, hole mobility decreased. In this study, we observed that the hole mobilities of the ternary active layers generally increased upon increasing the content of the CBS polymer up to 15% of the overall donor fraction. The higher carrier mobilities likely contribute to the higher J_{SC} observed in many of the ternary devices. The as-cast ternary solar cells made in ambient environment without any pre/post treatment gave strong performance up to 25% of CBS polymer loading. This work demonstrates that introducing highly stretchable CBS polymers with poor charge mobility does not adversely affect solar cell performance, offering insights into the development of ternary strategies for flexible/stretchable organic solar cells.

KEYWORDS: Ternary organic solar cells, Conjugated polymers, conjugation-break spacer, semi-random polymers, elastic polymers

Introduction:

Organic semiconducting polymers, in contrast to bulk inorganic semiconductors, are solution processable and offer the potential for cost-effective printing on flexible, large area substrates to generate flexible/stretchable electronics (such as wearable devices).[1] Both high charge carrier mobility and mechanical compliance are required for such applications.[2] Charge transport

mechanisms have been intensively studied in conjugated polymers (CPs) and great improvements have made in the last three decades.[3] However, a deep understanding and optimization of the mechanical performance of semiconducting polymers is still in its infancy.[4] Compared to high molecular weight commodity polymers, such as polyethylene or nylon, organic semiconducting polymers do not exhibit high strength and toughness.[5] For flexible/stretchable electronics applications, materials with low elastic modulus are required. It was shown that many conjugated polymers have considerable stiffness (elastic modulus varies widely in the range of 0.1 to 8 GPa).[6,7] In other words, compared to conventional elastomers such as poly(dimethylsiloxane) (PDMS) (E = 0.6–2.5 MPa) or polyisoprene (E = 0.36 MPa),[8] most fully conjugated polymers have poor mechanical properties, are brittle, and tend to fracture at low strains (<10%).[9] Thus, designing new organic semiconducting polymers and developing new strategies for multi-component systems that can effectively improve the electrical and mechanical properties of flexible, stretchable, and long-lasting organic electronics is of paramount importance. The physical properties of these materials should be optimized to yield high elasticity (low modulus) and a low glass transition temperature in order to increase mechanical ductility. High strength and toughness are also desirable.[10]

Several approaches have been explored toward this end. For example, it was shown that long and extended side chains can decrease the volume fraction of the stiff conjugated units and open up the space between polymer chains. Consequently, the elastic modulus is decreased which results in better mechanical properties of the semiconducting polymer.[11,12] Other than side chain engineering,[13,14] there are a few other approaches have been studied to increase the elasticity of semiconducting polymers, including introducing dynamic non-covalent (hydrogen bonding) or

soft crosslinkers,[7,15] nanoconfinement,[16,17] elastomeric matrices,[18,19] double-crystalline block copolymers[20] and controlling critical molecular weight.[21]

Recently, conjugation break spacers (CBS) were introduced to the field of organic electronics.[7,22–27] A CBS unit is a non-conjugated segment, such as a flexible alkyl chain that disrupts the conjugation along the polymer backbone. Initially, conjugation breakers were designed to improve processability of polymer semiconductors. Several studies have shown that incorporating flexible CBS units into conjugated backbones is an effective technique to modulate solubility,[28] solution processability[29] and even offers melt-processable semiconducting polymers,[30] which eliminates the need for toxic organic solvent for thin film formation. Another focus of CBS research is to improve mechanical properties and specifically, stretchability of conjugated polymers. Flexible linkages cause numerous degrees of conformational freedom and energetic disorder in polymer chains. Savagatrup et al. reported an improvement in ductility and modulus by increasing proportions of the nonconjugated unit in diketopyrrolopyrrole-based polymers.[27] The optoelectronic properties of multiple conjugated rigid segments that are linked by non-conjugated soft chains can be molecular weight independent. Li et al. showed that compared with a small molecule reference, rigid conjugated segments linked by non-conjugated soft segments had better photovoltaic performance by a factor of 29–73%.[31] The effect of backbone flexibility on n-type polymers with CBS units of varying lengths was studied by Gu et al. They showed that increasing the backbone flexibility leads to a softening effect that reduces the elastic modulus and increases ductility up to 400% strain with four carbons spacers.[32] Overall, it is clear that incorporation of CBS units into conjugated polymers has greatly impacted mechanical properties, where CBS polymers have consistently shown elastic moduli of less than

1 GPa. However, balancing this improvement and charge carrier mobility is nontrivial, and in many cases still remains a challenge.[7,27]

In the past two decades, organic photovoltaics (OPVs) have been considered as one of the best strategies for the sustainable production of electricity due to their advantages of solution processability, light weight and flexibility.[33] One aspect of OPV technology that needs to receive more attention is the mechanical properties of conjugated polymers and the changes in photovoltaic performance of devices under mechanical strain. Achieving high efficiency and robust mechanical properties simultaneously is quite challenging due to the fact that crystalline semiconducting polymers with high charge mobilities tend to be brittle.[12,34] In the first reported stretchable organic solar cells, an active layer was spin coated on a pre-strained elastomeric membrane (P3HT:$PC_{61}BM$ on PDMS substrate). The microscale wrinkles that formed upon release of the strain imparted elasticity to the device under tensile strain (up to 27%) with very little change in the photovoltaic properties.[35] To date, the highest PCE of flexible organic solar cells has reached above 12%.[36] However, there are few examples in the literature of intrinsically stretchable materials used for organic solar cells.[27,37,38] Savagatrup et al. studied the effects of CBS units on the mechanical and photovoltaic properties of a series of diketopyrrolopyrrole-based polymers. It was reported that the photovoltaic properties of DPP-based CBS polymers with $PC_{61}BM$ decreased with increasing ratio of the CBS units. The major challenge in utilizing CBS polymers in OPV arises directly from the competition between their electronic and mechanical properties where CBS content has been observed to have a negative impact on the charge carrier mobility of the polymer.[27]

Constructing ternary organic solar cells is a potentially convenient strategy to further enhance performance with CBS polymers. The concept of ternary organic solar cells initially was proposed as an effective strategy to boost the device performance by broadening the light absorption.[39] This was achieved by incorporating a third component with complementary absorption into a binary donor-acceptor host.[40] Later, many studies reported that a third component could also enable modulation of energy levels and film-morphology of the active layer in solar cells and demonstrated that the third component in ternary blends plays versatile functions.[41] In other words, the advantages of the third component can be reflected in the device performance and enhance short-circuit current-density (J_{SC}), open-circuit voltage (V_{OC}), and fill-factor (FF).[42–44] The performance of ternary devices considerably depends on the materials combinations that can form matched electronic structure and proper blend morphology for charge generation and transport.[45,46] Baran et al. reported that employing a third component into a low-bandgap:fullerene binary solar cell not only enhances the photovoltaic performance but also synergistically improves both storage lifetime and photo-stability.[47] Recently, Huang et al. reported that the mechanical properties of a ternary blend of PBDTTT-OFT:IEICO-4F:$PC_{71}BM$ were superior to the corresponding binary devices.[48] This is typically due to the fact that compared with conventional polymer fullerene solar cells, non-fullerene acceptors (NFA) and especially polymer acceptors are intrinsically more ductile than fullerenes.[49] They claimed that using $PC_{71}BM$ at low ratios decreased the crystallinity of the host acceptor and no pure $PC_{71}BM$ aggregation (which leads to brittleness) was observed in the ternary blend. Similar results were reported by Geng et al. using $PC_{71}BM$ at a low ratio in a polymer:small molecule acceptor blend, although the elastic modulus increased, the crack-onset strain improved slightly from 7.1 to 9.3 %.[50]

Based on the current deficiencies in stretchable OPV, we were motivated to investigate a class of highly ductile semi-random CBS polymers previously developed in our group[12,34] as components in ternary blend OPV. Our focus is to elucidate the impact of the CBS polymers on the electronic device characteristics of the solar cells to validate whether such an approach has the potential to lead to high performance solar cells. Here we have focused on ternary blends based on a fully conjugated polymer, a CBS polymer, and $PC_{61}BM$, with the understanding that fullerene-based OPV will likely not have strong mechanical properties,[51,52] but rather with a focus on demonstrating if adding CBS polymers (with inferior electrical properties) can be tolerated with retention of device performance and thus could potentially provide a route to solar cells with intrinsically stretchable active layers. The idea of introducing these CBS polymers into a fully conjugated polymer:fullerene binary system is to provide a pathway to active layers with enhanced mechanical deformability for stretchable OPV. In order to design our ternary systems, we have considered to employ donor polymers with good chemical structure compatibility, as incompatibility between the host and the guest components could disturb the optimized morphology of the donor/acceptor binary blend active layer.[53,54]

In our previous studies we synthesized polymers with CBS units in 3-hexylthiophene-DPP based semi-random polymers and we examined several different classes. Members of these classes selected for this study are shown in **Scheme 1**.[12,34] These CBS polymers have variety of properties, such as mechanical, morphological, electrical, electronic, structural (side chains, CBS and DPP ratios, molecular weight), etc. In this study, we chose a broad range of CBS polymers with a wide range of properties while keeping one variable constant. Here we focus only on CBS polymers with 8-carbon alkyl spacers. In class I, the CBS content was varied concurrently with the DPP monomer content (with 2-ethylhexyl (eh) side chains) at 10% and 20% with a

corresponding 3-hexylthiophene content of 80% and 60%. For this class of polymers, it was shown that with 10% of 8-carbon alkyl spacer, the elastic modulus was decreased from 0.32 GPa with the fully conjugated analogue (P3HTT-ehDPP-10%, **Scheme 1**) to 0.14 GPa and crack-onset strains (COS) increased from 10% to >80% (using the film-on-elastomer technique). Compared to the fully conjugated analogue, the hole mobility decreased from 9.29 x 10^{-4} cm^2 V^{-1} s^{-1} to 2.08 x 10^{-5} cm^2 V^{-1} s^{-1}. By increasing the content of spacer to 20%, the elastic moduli increased to 0.65 GPa, while COS remained >80% and mobility dropped one more order to 6.49 x 10^{-6} cm^2 V^{-1} s^{-1}. Overall, the mode of failure for this class of polymers is ductile (compared to the brittle conjugated parent polymer) and more notably, the beneficial properties of P3HT such as absorption and electronic energy levels were largely retained.[34] The highest occupied molecular orbitals (HOMO), compared to the fully conjugated polymer, were slightly upshifted and the band gap (E_g) saw similar minor shifts to higher energy (**Table S1** includes HOMO and E_g data for all polymers).

When the side chain on the DPP monomer was replaced with 2-decyltetradecyl (dtd) (Class II, **Scheme 1**, the solubility was improved, and higher molecular weights were obtained (molecular weight data for all polymers in **Scheme 1** are shown in Supplementary **Table S1**). These polymers achieved remarkable mechanical properties. For example, with 20% of CBS monomer in the polymer chain, an elastic modulus of 15.07 MPa was measured along with a fracture strain of 185% (using the film-on-water technique). By increasing the CBS ratio to 30% and 40%, elastic moduli of 14.84 and 27.39 MPa were obtained, respectively, while fracture strains increased to a remarkable 325% and 398%, respectively. Predictably, these structures with outstanding mechanical properties resulted in diminished electrical properties. Compared to the fully conjugated dtdDPP parent polymer (analogous to P3HTT-ehDPP-10%), the hole mobility

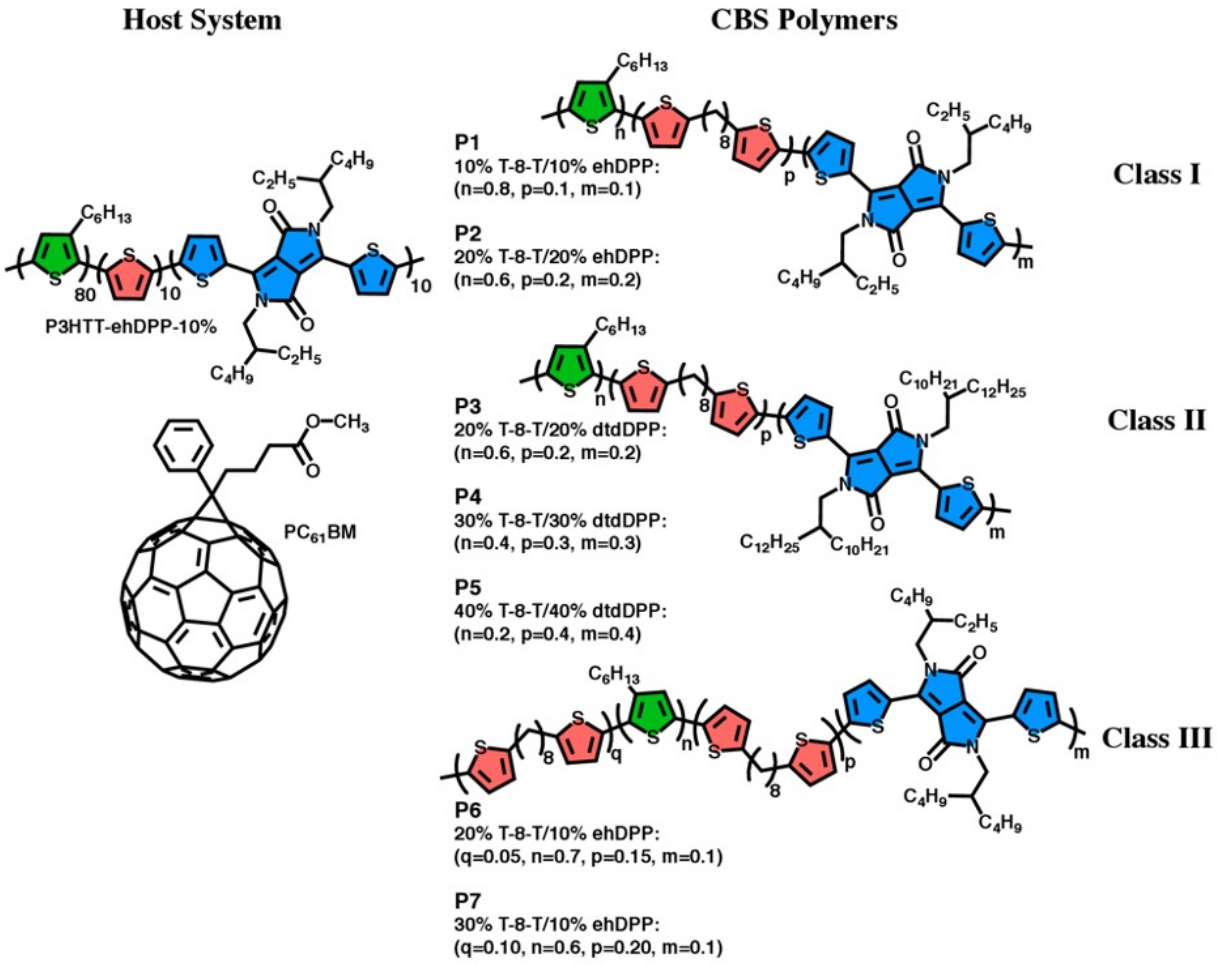
decreased more than one order from 4.24 x 10^{-4} cm^2 V^{-1} s^{-1} to 1.01 x 10^{-5}, 6.22 x 10^{-6} and 4.92 x 10^{-6} cm^2 V^{-1} s^{-1} for 20%, 30% and 40% of CBS loading, respectively.[12]

Finally, in the third class of polymers, the ehDPP monomer content was fixed at 10 mol %, and the CBS monomer was incorporated at 20% and 30% while corresponding 3-hexylthiophene content was at 70% and 60%, respectively. Extremely high ductility was achieved in this class of polymers at the cost of electrical properties. With 20% and 30% of CBS in these polymers, elastic moduli of 52.7 and 8.54 MPa were obtained, respectively, while fracture strains were measured at 200% and 432%, respectively (film-on-water).[12] The hole mobility of this class of polymer dropped from 9.29 x 10^{-4} cm^2 V^{-1} s^{-1} to 7.05 x 10^{-6} cm^2 V^{-1} s^{-1} and 2.06 x 10^{-6} cm^2 V^{-1} s^{-1} when 20% and 30% of CBS were incorporated into the polymer, respectively.[12] Evaluation of these series of polymers leads to the conclusion that there is a trade-off between mechanical and electrical properties and that the more ductile these polymers become, the worse the charge carrier mobility becomes.

All of the CBS polymers in **Scheme 1** were initially tested in in binary solar cells with $PC_{61}BM$ as the acceptor. Likely due to their deficient hole mobility, the binary device performances were extremely poor. For example, for an optimized P1:$PC_{61}BM$ binary system (Class I), the highest PCE achieved was 0.7% (J_{SC}=3.2 mA cm^{-2}, V_{OC}=0.65 V, FF=34, **Table S2**). As such, we sought to study the unique functionalities of these polymers in ternary organic solar cells and investigate the device performances by incorporating the CBS polymers into a fully conjugated polymer host system (**Scheme 1**) based on P3HTT-ehDPP-10% and $PC_{61}BM$. To the best of our knowledge, this is the first ternary solar cell study incorporating intrinsically ductile CBS polymers. In the current work, our focus is on establishing the potential of this avenue by

presenting a model system containing a fully conjugated polymer, a CBS polymer and $PC_{61}BM$. We emphasize that although introducing some of our CBS polymers into binary blends results in enhanced performance, these results may not necessarily be obtained with all CBS polymers.

Scheme 1. Chemical structures of P3HTT-ehDPP-10% (parent donor polymer), $PC_{61}BM$ as the acceptor and CBS donor polymers used in this study.



Results and discussion:

Photovoltaic performance

To evaluate the potential of these polymers in OPV, ternary bulk heterojunction solar cells were fabricated with an ITO/PEDOT:PSS/conjugated polymer:CBS polymer:$PC_{61}BM$/Al conventional device architecture. All of the devices were fabricated and characterized in air. The *J-V* characteristics of the devices were measured at an active area of 5.18 mm^2. *O*-dichlorobenzene (o-DCB) was used as the solvent with the overall polymer concentration of 10

mg/mL. For all devices the weight ratio of donors:$PC_{61}BM$ was kept constant at 1:1.3. For ternary devices, CBS polymers were added at 10%, 15% and 25% of the total donor polymer fraction. Higher ratios of CBS (up to 50%) were tested for some CBS polymers (**Table S2**). However, adding more than 25% of CBS in the ternary blend was observed to deteriorate the device performance sharply. Therefore, here we focus on the photovoltaic properties of ternary devices with up to 25% CBS polymer in the donor fraction. The photovoltaic performance data including V_{OC}, J_{SC}, FF, and PCEs for host binary and ternary devices are summarized in **Table 1**. The J_{SC} values were well matched (within 5% error) with the integrated J_{SC} values obtained from the EQE spectra (see **Table S3** for the mismatch factor and J_{EQE}). The average PCE of the fully conjugated P3HTT-ehDPP10%: $PC_{61}BM$ reference was 4.35% over 25 pixels (V_{OC}=0.6 V; J_{SC}=10.8 mA cm^{-2}; FF=55.1). Upon introducing the CBS polymers of Class I, P1 and P2, the efficiency was observed to decrease in both cases as the content of the CBS polymer increased in the system. Predictably, we attribute losses in efficiency primarily to the fact that the optoelectronic properties of these CBS polymers are inferior to the fully conjugated parent, which leads to decreases in the J_{SC} and FF, especially at high contents.[34] Since the hole mobility of P2 is lower than P1, it is possible that devices containing the former experienced a greater decrease in efficiency than the latter. However, there is no absolute correlation between CBS polymer mobility and ternary solar cell performance observed in this work.

Table 1. Photovoltaic properties of ternary P3HTT-ehDPP-10%:CBS:$PC_{61}BM$ Solar Cells.

CBS polymer	Composition P3HTT-ehDPP-10%:CBS:$PC_{61}BM$[a] (% CBS in polymer fraction)	J_{SC} (mA/cm^2)[b,c]	V_{OC} (V)	FF	Average PCE (%)[d]	Crack-onset strain (COS) (%)[12,34]
P3HTT-ehDPP-10% (reference)	1:0:1.3	10.8	0.60	55.1	4.35	10 [f]
P1 (ClassI)	0.9:0.1:1.3 (10%)	9.56	0.61	52.4	3.92	>80 [e,f]
	0.85:0.15:1.3 (15%)	9.56	0.59	48.9	3.55	
	0.75:0.25:1.3 (25%)	8.25	0.60	48.4	3.09	
P2 (ClassI)	0.9:0.1:1.3 (10%)	9.47	0.59	50.8	3.66	>80 [e,f]
	0.85:0.15:1.3 (15%)	9.55	0.57	46.4	3.15	
	0.75:0.25:1.3 (25%)	8.27	0.58	44.3	2.68	
P3 (ClassII)	0.9:0.1:1.3 (10%)	10.00	0.59	52.4	3.94	185 ± 26 [g]
	0.85:0.15:1.3 (15%)	10.98	0.59	52.7	4.36	
	0.75:0.25:1.3 (25%)	8.44	0.59	48.1	3.12	
P4 (ClassII)	0.9:0.1:1.3 (10%)	10.60	0.59	54.3	4.32	325 ± 44 [g]
	0.85:0.15:1.3 (15%)	10.30	0.59	51.2	4.00	
	0.75:0.25:1.3 (25%)	10.30	0.60	52.7	4.21	

P5 (ClassII)	0.9:0.1:1.3 (10%)	10.70	0.60	58.1	4.82	398 ± 32 [g]
	0.85:0.15:1.3 (15%)	9.30	0.59	55.1	4.05	
	0.75:0.25:1.3 (25%)	9.83	0.59	49.7	3.85	
P6 (ClassIII)	0.9:0.1:1.3 (10%)	9.27	0.60	53.2	3.70	200 ± 5 [g]
	0.85:0.15:1.3 (15%)	9.54	0.60	53.7	3.89	
	0.75:0.25:1.3 (25%)	8.90	0.60	49.2	3.33	
P7 (ClassIII)	0.9:0.1:1.3 (10%)	7.39	0.59	45.9	2.56	432 ± 38 [g]
	0.85:0.15:1.3 (15%)	8.87	0.61	51.8	3.52	
	0.75:0.25:1.3 (25%)	11.04	0.60	54.9	4.60	

[a] All devices were spin-coated from o-dichlorobenzene (o-DCB) and dried under N_2 for 30 min before aluminum deposition. [b] Mismatch corrected. [c] Standard deviations of less than 0.5 mA/cm^2 were observed in all cases averaged over six to twenty-five pixels. [d] STD deviations are given in table S3 in the SI. [e] Obtained from optical micrographs, film-on-elastomer measurements from neat polymers. [f] Test terminated at 80% strain due to potential for PDMS substrate breakage. [g] Obtained from strain at failure, film-on-water measurements from neat polymers

With class II CBS polymers, the 2-ethylhexyl side chains on DPP are replaced by 2-decyltetradecyl. In the ternary blends, the addition of the Class II CBS polymers does not decrease the J_{sc} as much as the Class I polymers and the average current in this set of ternary devices is higher, especially at lower CBS contents. For example, by addition of 15% of P3, the current is slightly higher than the binary reference system. The higher current in this set could possibly be attributed to the higher molecular weight of this family of polymers (see **Table S1**). With P4 even up to 25% CBS polymer incorporation resulted in almost the same performance

compared to the fully conjugated reference binary system. This means that incorporation of a CBS polymer into the host did not inhibit the system, despite the poorer electrical properties of the CBS, even up to 25% composition.

While there is no direct correlation between the CBS polymer mobility and J_{SC} in this class, we do observe that for P5 (with the lowest hole mobility in Class II of 4.92 x 10^{-6} cm^2 V^{-1} s^{-1}) at 10% incorporation of this CBS polymer into the binary system, the device efficiency (4.82%) actually exceeds the reference binary (4.35%). As such, adding 10% of a highly ductile polymer with an inadequate hole mobility could actually make a binary device work better. However, higher content of this polymer resulted in decreasing current and efficiency. In this class, we also observed that at low fraction of CBS polymer in the ternary blend (10%), the current, FF and PCE increase as the CBS content in the polymer backbone increases from 20 to 30 to 40%. No corresponding trend was observed for the 15% ternaries. In the 25% blends, J_{SC}, FF and PCE are maximum for P4. Hence, although CBS polymer mobility in this class decreases as the CBS content increases in the polymer backbone, it cannot be directly translated to the ternary device performance.

Lastly, with the Class III CBS polymers, addition of P6 follows a similar trend observed in the previous CBS Classes. Although the overall current, FF and efficiency of the ternary devices are lower than the binary, the ternary devices are still functional up to 25% content of the CBS polymer. All J-V (**Figure S1-S7**) and EQE (**Figure S8-S14**) curves are shown in SI. Surprisingly, addition of P7 showed the opposite trend compared to the previous CBS polymers, where increasing the content of the CBS polymer resulted in an increasing PCE and an efficiency exceeding the binary reference (4.60 vs. 4.35%) was achieved when incorporating 25% of this polymer. **Figure 1a** shows the current density versus voltage (J–V) curves with a flux of 100

mW/cm^2 under simulated AM 1.5G conditions and **Figure 1b** shows the external quantum efficiency (EQE) of the optimized ternary solar cells with P7 at different donor ratios. At the ratio of 25% CBS, the EQE values of ternary devices are higher than the binary reference in the low energy region of 600-800 nm, but lower in the high energy region of 400-600 nm. As indicated in **Table 1**, this polymer showed the highest fracture strain (over 430%) which is among the highest reported for conjugated polymers. Although in Class I, going to higher CBS content results in lower PCE at each composition (10, 15, and 25%), the same trend was not observed with Class II and Class III. This is not surprising considering that each class has a structurally distinct motif.

While no universal correlations were found across the different CBS classes between properties and performance parameters, we do observe these general points: First, the J_{SC} peaked at 15% composition in ternary blends for all 20% CBS polymers (P2, P3 and P6). This trend was not present for other ratios of CBS (for example for 30% CBS). Second, although comparable values of J_{SC} were obtained for most of the ternary devices, our results demonstrate that CBS polymers with dtd side chains on DPP generally showed higher J_{SC} and FF. One hypothesis is based on the side chains on the CBS polymers being longer than the side chains on the host polymer. This could result in modulating the morphology to generate an interpenetrating mesoscale polymer domain based on similar results reported by Chang et. al.[42] In their work, a ternary blend with two polymer donors with nearly identical absorption spectra and similar energy levels were used. However, the side chains on their D1 and D2 were oriented differently. They proposed that introducing the second donor to the binary system improved the morphology from nanoscale (10–20 nm) fine fibrils to a meso scaled morphology, in which the donor domain volume swelled after adding D2, coupled with reduced donor phase crystallinity in the ternary blend. The better

charge collection and higher J_{SC} they observed were attributed to the resulting interpenetrating network of the donor and acceptor phases. Overall, though, the ternary solar cell results presented here demonstrate that addition of up to 25% CBS polymer in the donor fraction leads to functioning devices with similar and sometimes improved performance. This bodes well for the future use of this strategy in flexible/stretchable OPV.

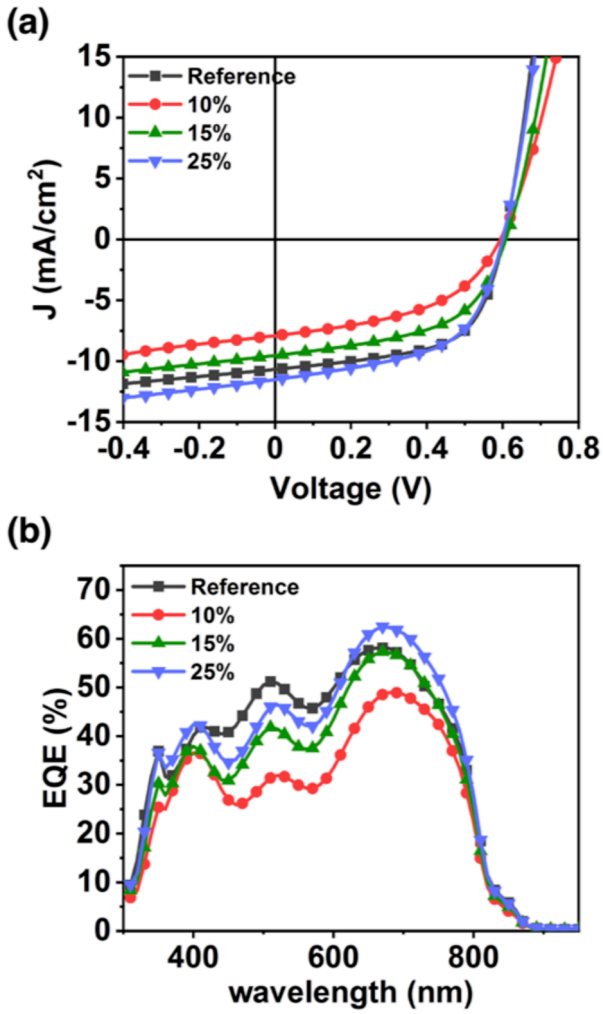


Figure 1. (a) J–V curve and (b) EQE spectra of ehDPP-10%:P7:$PC_{61}BM$. P3HTT-ehDPP-10%:$PC_{61}BM$ J-V curve and EQE spectrum provided for fully conjugated reference.

Morphology and Charge Carrier Mobility

As we have thoroughly interrogated the parent system (P3HTT-ehDPP-10%:$PC_{61}BM$) morphology in our previous work,[55,56] and considering the similar structures of the CBS polymers and the host polymer in these model systems, in this study only limited morphology characterization was pursued. Crystallinity in as-cast ternary blend films was examined by grazing incidence x-ray diffraction (GIXRD). GIXRD data for all neat CBS polymers was previously reported.[12,34] The GIXRD data showing the 100 diffraction peaks corresponding to the polymer lamellar packing for all ternary active layers are shown in **Figure S15-S21** and **Table S4**. For crystallite size determination, the Scherrer equation was applied using integral width of the diffraction profile. It is noteworthy that the shape factor constant (here we used 0.9) in this equation can be affected by several factors, including the finite grain size, grain size relative to the film thickness, shape of grains (e.g., spherical vs cylindrical), and the effect of the final resolution in experimental measurements, hence this equation should be used with additional care.[57] Compared to the fully conjugated binary reference system, all ternaries showed an increase in the lamellar packing distance. Due to our similar film compositions and thicknesses (Table S4), we will make the rough correlation that increasing intensity of GIXRD data corresponds to greater crystallinity.[58] Surprisingly, in ternary blends constructed with Class I CBS polymers, for all ratios, a higher intensity peak was observed compared to the fully conjugated DPP:$PC_{61}BM$ blend, indicating enhanced crystallinity relative to the binary reference. In our previous studies, we showed that this class of polymer exhibited a lower intensity diffraction peak compared to P3HTT-ehDPP-10%. Although, introducing the third component into a binary system may disturb the crystallinity of both donor and acceptor phases,[48] many studies reported that the optimized morphology, in terms of molecular crystallite

orientation and aggregation, can be maintained[54] or enhanced[59] in ternary blends. This could be due to the structural similarity and compatibility between the third component with the host donor or acceptor.[53,60] However, it is quite rarely reported that the crystallinity of the ternary active layer is improved by a less crystalline component.[61] The intensity of the peak is highest for the 10% blend and decreased at 15% and 25% ratios.

In contrast, with Class II CBS polymers, except for the cases of 10% of P3 and P4, the diffraction peak for all ternary blends was decreased compared to the fully conjugated binary reference. However, the lamellar packing distance increased even more compared to Class I. It is likely that the longer alkyl side chains on the DPP units of the CBS have a more disruptive impact on the morphology. The *highest* J_{SC} in Class II was achieved at 15% of P3 (10.98 mA cm^{-2} which shows 1.7% improvement compared to the binary reference) with crystallinity slightly lower than the reference. In ternary systems with P5, although all peak intensities are lower than the reference, at 10% content the current is almost as high as the reference binary cell (10.7 mA cm^{-2}). The more significant changes in morphology induced by Class II polymers, coupled with improved device performance relative to Class I, suggests that the switch from eh to dtd side chains may have a similar impact as in the work reported by Chang et. al[42] noted earlier.

In the third class of CBS polymers, except for the 10% ternary blend of P7, all ternary films showed higher intensity peaks than the DPP:$PC_{61}BM$ binary reference. The GIXRD patterns for P7 ternary blends are shown in **Figure 2**. The peak intensity at 10% CBS in the blend is slightly lower than the fully conjugated reference sample. For this polymer with good structural compatibility with the host (10% ehDPP in both polymers) and the highest amount of CBS

(30%), the intensity of the lamellar peak increases by addition of CBS polymers in the system, where 15 and 25% incorporation of the CBS polymer shows a significant enhancement in crystallinity relative to 10% incorporation and the reference binary. Although, the lamellar packing distance is increased compared to the binary cell, increasing the content of CBS polymer in the system (from 10% to 25%) does not change the d_{100}. It is possible that the increasing crystallinity of this ternary blend leads to increased J_{SC} for this particular system.

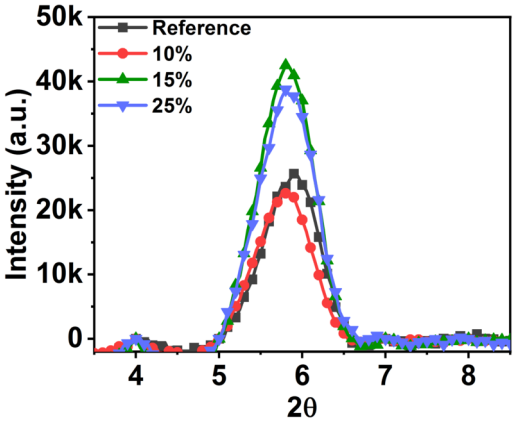


Figure 2. Grazing-incidence X-ray diffraction patterns of P3HTT-ehDPP-10%:P7:$PC_{61}BM$ thin films spin-cast from o-dichlorobenzene (o-DCB) and dried under N_2 for 30 min. P3HTT-ehDPP-10%: $PC_{61}BM$ data provided for fully conjugated reference.

Although introducing a third component has proven to be an effective way to enhance the photovoltaic performance compared with binary devices in many cases, rationally designing a miscible component for the host binary system to achieve a well-developed morphology is quite challenging.[64–66] Peng et al. reported that synergistic effects of two structurally compatible components with good miscibility enhanced the charge transport in a ternary system.[67] Our

results demonstrate that constructing ternary devices by incorporating structurally similar polymer donors is an effective strategy to maintain (for example in P1 and P3 systems) and further improve (in P7 system with 25% of CBS) the photovoltaic performances of the devices.

Space-charge limited current (SCLC) mobility measurements were performed on hole-only devices for all the ternary blend samples and the binary reference (**Figure 3** and **Table S5)**. Although all CBS polymers showed significantly lower hole mobility compared to the fully conjugated parent polymer, it could be expected that the ternary active layers would show similar mobility to the fully conjugated binary reference blend. Mei et al. has shown that in complementary semiconductor blends of CBS polymers, only a few percent of a fully conjugated polymer (as little as 1 wt%) is needed to induce a nearly 2 order of magnitude improvement in the charge carrier mobility of the blend.[68–70] Our findings provide a quantitative verification that increased ratio of CBS polymers in the blend does not undermine hole transport. However, not all blends resulted in the same mobility as the binary reference. A similar trend in hole mobilities of the ternary blends was observed in most cases. Specifically, the hole mobility for the CBS ternary blends was generally observed to increase when the composition increased from 10% to 15% of the donor fraction and then decrease at the higher loading of 25%.

With the Class I CBS polymers, the ternary devices with P1, in which CBS polymers had the lowest fraction of spacers, showed lower hole mobility compared to the reference binary for all ratios. With P2, while the same trend was observed, for this ternary system at 15% content, the mobility is comparable to the binary reference. Since both P1 and P2 ternary blends show similar crystallinity, higher mobility in the latter system could be attributed to the higher content of DPP in P2 polymer.

With the Class II CBS polymers, the same general trend, in which mobility was increased up to 15% content and then decreased, was observed. Moreover, it is clear that as the content of the CBS in the polymers is increased (from 20 to 30 to 40%), the mobility of the ternary blends decreased. It was found that the 15% blends of the P3 polymer could enhance the mobility relative to the binary reference. In this particular device, all photovoltaic parameters are very similar to the P3HTT ehDPP10%:$PC_{61}BM$ reference. Note that the GIXRD pattern for P3HTT-ehDPP10%:P3:$PC_{61}BM$ at 15% is almost the same, in terms of intensity, as the binary reference. Meaning that the optimized binary morphology was maintained and this polymer at this ratio did not perturb the host system. However, such correlations do not extend across all ternary blends tested in this work. The mobility in ternary devices with P4 does not follow the general trend, however, it is still comparable with the binary reference up to 15%. The calculated crystallite size at 15% with this polymer is exactly the same as the binary reference (9.98 nm, **Table S4**). Although the crystalline correlation length (CCL) was slightly lower than the binary, which could be due to the morphology disturbance, similar crystallite size could have resulted in similar mobilities compared to the binary (1.01 x 10^{-3} cm^2 V^{-1} s^{-1} and 1.22 x 10^{-3} cm^2 V^{-1} s^{-1}, respectively). The lowest charge mobility for the devices were observed for P5 which has the highest fraction of CBS.[29]

For the Class III CBS polymers, the trend in P6 is quite different than the general trend. Here, the mobility for ternary devices reached the highest value at 25% (1.72 x 10^{-3} cm^2 V^{-1} s^{-1}). In P7 ternaries, the difference between charge mobilities at 15% and 25% is very small (0.2 cm^2 V^{-1} s^{-1}) and the highest current achieved for all ternary solar cells (11.04 mA cm^{-2}) belonged to P3HTT-ehDPP10%:P7:$PC_{61}BM$ at 25%. The mobility values for this device and the reference are the most similar among all other blends (**Table S5**, 1.18 x 10^{-3} and 1.22 x 10^{-3} cm^2 V^{-1} s^{-1},

respectively). As mentioned earlier, although no absolute correlation was found between different CBS polymer mobilities and J_{SC} in general, better electrical properties in this ternary blend could have contributed to achieving higher current.

In this study we observed a general trend (with a library of CBS polymers and a wide range of properties) that the mobility for ternary devices reaches its maximum at 15% CBS fraction in the blend (with the exception of P4 and P6). Although drawing a universal conclusion correlating electrical, morphological and photovoltaic properties is elusive, we have observed some general trends: First, as mentioned in the introduction, the mechanical properties of CBS polymers were enhanced by increasing the CBS content. For the CBS polymers with the best mechanical properties in each class (P2, P5 and P7), we have shown that the optimum composition ratio in the ternary blend is 15%, which leads to the highest crystallinity and mobility. Second, in terms of hole mobility only, in each class, it was shown that ternary devices with CBS polymers containing 20% of break spacers, have overall better mobilities. While more investigation is necessary in order to correlate the efficient charge transport and the degree of disorder in these systems with OPV performance, we have observed that the PCE values reached the maximum with 10-15% loading in nearly all cases (with the exception of P7).

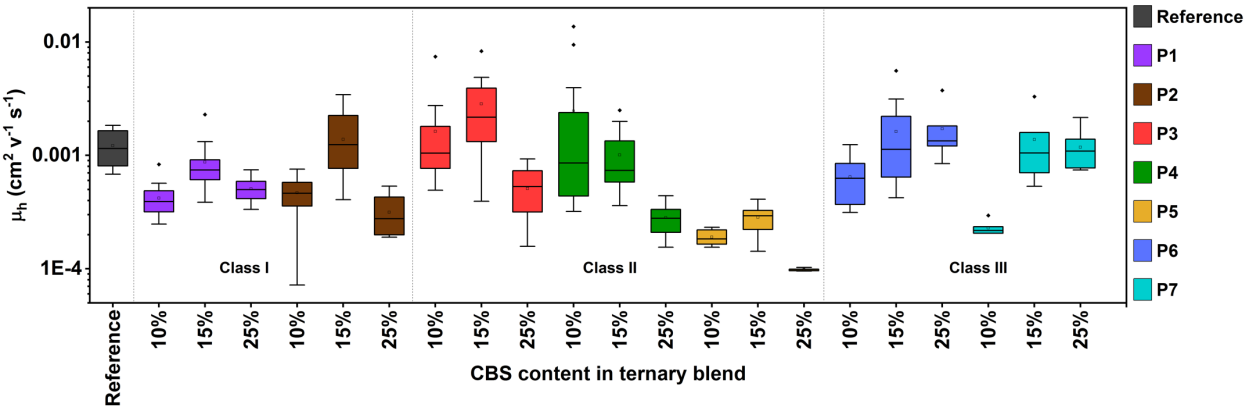


Figure 3. Hole mobility trends in P3HTT-ehDPP-10%:CBS:$PC_{61}BM$ ternary blends at different donor ratios.

Conclusions:

Here, seven CBS polymers were successfully incorporated into ternary blend solar cells based on a fully conjugated polymer:$PC_{61}BM$ binary reference system. The purpose of this study is to demonstrate that highly ductile CBS polymers can be incorporated into solar cells without inhibiting device function. Although the focus of this work was not on the mechanical properties of the active layers (and would likely not be relevant with a fullerene acceptor), we have presented a model system demonstrating the potential for CBS polymers to be used in ternary blends. We have successfully shown that structurally similar ductile polymers, with a range of motifs (e.g., different side chains, DPP content, CBS ratio in blend), can all be incorporated into a fully conjugated polymer based binary system. Not only does the host system largely retain its performance, but also in some cases the ternary blends slightly out-perform the reference. Thus, we have demonstrated the potential of this strategy. It was observed that 25% donor content of P7 showed better performance than the fully conjugated reference binary blend. This polymer

also has the highest fracture strain (432%) among the CBS polymers investigated here. Although CBS polymers suffer from poor mobility in neat films, they can occupy a significant fraction of the active layer of a solar cell without compromising electrical properties.

Our results indicate that employing CBS polymers in a ternary blend is a potentially promising route to advance mechanical properties in polymer-based solar cells. Although PCE in the present examples is low, this strategy opens an avenue for further development of ternary blends with both electrical and mechanical function. Such a strategy could enable a method to rationally transform a binary system into an enhanced ternary blend with improved mechanical properties. However, to envision the true potential of this proposed strategy, brittle fullerenes must be replaced with ductile polymer acceptors, which will be the focus of our future research. Moreover, our future studies will aim to correlate the impact of spacer length and side chain identity of the CBS polymer with the device performance, where the film morphology and mechanical property relationship will be emphasized. This work is aimed to provide insight into promoting stability and robustness in organic solar cells.

Supporting Information Available:

General procedures, materials, and characterization methods, spectral mismatch correction, EQE, mobility and *J-V* data, GIXRD patterns and data; SCLC hole mobility data. The Supporting Information is available free of charge on the ACS Publications website (PDF).

Corresponding Author

*Barry C. Thompson (barrycth@usc.edu).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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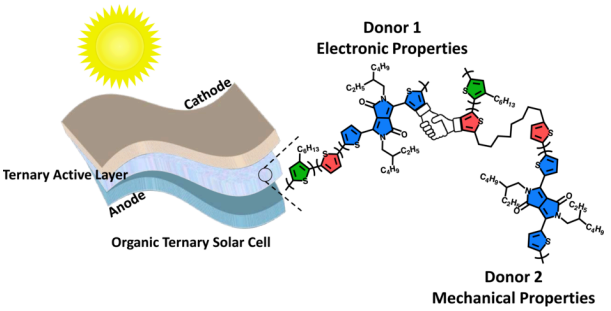
TOC GRAPHIC


Donor 1
Electronic Properties
Cathode
Ternary Active Layer
Anode
Organic Ternary Solar Cell
Donor 2
Mechanical Properties