High-performance multiple-donor bulk heterojunction solar cells

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Broadening the absorption bandwidth of polymer solar cells by incorporating multiple absorber donors into the bulk-heterojunction active layer is an attractive means of resolving the narrow absorption of organic semiconductors. However, this leads to a much more complicated system, and previous efforts have met with only limited success. Here, several dual-donor and multi-donor bulk-heterojunction polymer solar cells based on a pool of materials with different absorption ranges and preferred molecular structures were studied. The study shows clearly that compatible polymer donors can coexist harmoniously, but the mixing of incompatible polymers can lead to severe molecular disorder and limit device performance. These results provide guidance for the general use of multiple-donor bulk heterojunctions to overcome the absorption limitation and achieve both high performance and fabrication simplicity for organic solar cells.

Polymer photovoltaic cells have shown great potential as a means to harvest solar energy in a highly processable and cost-effective manner¹⁻⁵. Typical organic solar cells consist of a mixture of a polymer (or organic small molecule) donor and a C₆₀ derivative acceptor as the photoactive layer. In bulk-heterojunction (BHJ) organic solar cells, the absorbed incident photons generate tightly bound electron-hole pairs, which then dissociate into electrons and holes at the nearby donor/acceptor interface. The electrons and holes are then transported to their respective electrodes⁶⁻⁸.

Research efforts in the last decade or so have significantly improved organic solar cell performance⁹⁻¹⁴, and power conversion efficiency (PCE) values better than 10% have recently been achieved^{15,16}. Over the years, significant research efforts have been directed at developing low-bandgap polymers to extend absorption and harvest more solar energy. However, unlike the continuous band structure of inorganic semiconductors like Si, the molecular orbital energy level of organic or polymeric semiconductors is narrow, which makes it challenging to obtain panchromatic absorption coverage with a single organic semiconductor (Fig. 1). This is one of the reasons why polymer solar cells invariably exhibit a low short-circuit current (J_{sc}) compared with commercial inorganic solar cells. In addition, it has been very difficult to achieve external quantum efficiencies (EQEs) in low-bandgap polymer systems $(E_{\alpha} < 1.4 \text{ eV})$ that are as high as in traditional polymer systems such as poly(3-hexyl thiophene) (P3HT), for which EQE values of over 70% have been reported¹⁷. However, even with their imperfections, this rich set of low-bandgap polymers will have great value in efforts to improve state-of-the-art polymer solar cells if we can design organic photovoltaic (OPV) devices with multiple compatible polymers to expand the absorption range while at the same time maintaining other key parameters, such as open-circuit voltage $(V_{\rm oc})$ and fill factor (FF).

Unfortunately, very few successful ternary BHJ polymer photovoltaic cell structures have been reported that have efficiencies that surpass those of their corresponding binary BHJ devices¹⁸. The ideal scenario is that the multiple polymers will work independently. However, in reality, interactions between the two polymers are inevitable because of their different chemical and physical natures. These unfavourable interactions might function as 'morphological traps' and recombination centres, which lead to reduced photovoltaic performance in complex multiple-donor BHJ systems. Recent progress in the development of new photovoltaic materials has made available a wide pool of high-performance donor polymers with different absorption ranges. These have been widely used in OPV research and include poly[4,8-bis-substitutedbenzo[1,2-b:4,5-b]dithiophene-2,6-diyl-alt-4-substituted-thieno [3,4-b]thiophene-2,6-diyl] (PBDTTT-C) with $E_g = 1.60 \text{ eV}$, poly {2,6-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,4-b]dithiophene-alt-5dibutyloctyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-c]pyrrole-1, 4-dione} (PBDTT-DPP) with $E_g = 1.46 \text{ eV}$, poly{4,6-(2-ethylhexyl-3fluorothieno[3,4-b]thiophene-2-carboxylate)alt-2,6(4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*]dithiophene)} (PTB7) with $E_g = 1.62 \text{ eV}$, (poly{2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,4-b]dithiophenealt-2,5-bis(2-butyloctyl)-3,6-bis(selenophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione} (PBDTT-SeDPP) with $E_g = 1.38$ eV, and P3HT with $E_g = 1.90 \text{ eV}$ (refs 10, 19–23). It is well known that different highperformance polymers have their own preferred morphologies in the active layer, including their molecular orientation with respect to the substrate, crystallinity and domain size. For instance, regioregular P3HT tends to form edge-on lamellae in P3HT:PCBM films and exhibits much higher crystallinity than most other donor polymers; both properties are linked to its high photovoltaic performance^{17,24}. On the other hand, in many of the newer highperformance donor polymers such as thienothiophene (TT) and benzodithiophene (BDT), as well as BDT- and N-alkylthieno [3,4-c]pyrrole-4,6-dione (TPD)-based co-polymers^{20,25-27}, the preferred orientation to the substrate is face-on^{20,27,28}. This packing orientation is considered to be more advantageous to hole transportation in vertical diode configurations such as those used in photovoltaics^{28,29}. In addition, most of these newer polymers show significantly more amorphous character in their films than P3HT²⁸. We speculate that the use of two blended polymers with compatible physical natures (including molecular orientation and crystallinity) leads to less interference when forming the morphology of the BHJ

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Figure 1 | Band structure, band position and absorption spectrum of the model materials used. **a**, General schematic of the band structure of organic/polymeric and inorganic semiconductors. VB, valence band; CB, conduction band. **b**,**c**, Absorption spectra (**b**) and energy band diagrams (**c**) of the material pool.

active layers. Intuitively, the compatibility of their physical properties might strongly relate to similarity in their chemical structures.

In this Article we focus on identifying key parameter(s) for designing multi-polymer/fullerene derivative blends based on their individual structure-property relationships. The ternary polymer blend/fullerene systems studied here each have a highbandgap polymer and a low-bandgap polymer in order to cover a broader section of the solar spectrum. Figure 1 and Supplementary Fig. 1 present the model materials investigated in this study, all of which have previously been reported as high-performance photovoltaic materials featuring different absorption ranges and different molecular stacking preferences. For example, PBDTTT-C and P3HT both have demonstrated high EQE and PCE values, but one prefers edge-on and the other face-on orientation. These photovoltaic materials have been reported to have good device performance, but substantially different processing methods. Choosing a solvent that is compatible with each material is a particularly difficult challenge. PBDTTT-C and PTB7 generally work best when deposited from chlorobenzene (CB), with efficiencies of 6.58% and 7.4%, respectively, and their performance is slightly reduced when processed in dichlorobenzene (DCB)^{10,21}. However, polymers PBDTT-DPP and PBDTT-SeDPP are not sufficiently soluble in CB to form uniform films, so they are normally processed from DCB^{19,23}. To balance these ideal processing differences and set up an appropriate baseline, all the BHJ devices discussed here were fabricated using DCB as solvent.

In the material pool shown in Fig. 1, regio-regular (RR)-P3HT has an absorption edge around 650 nm and is expected to be spectrally matched to PBDTT-DPP and PBDTT-SeDPP. The devices with blended polymers present a much broader photocurrent response (Supplementary Fig. 2), but do not produce an overall enhancement in the photocurrent due to significant reductions in EQE. Additionally, the FF decreases markedly from ~65% to less than 40% in the mixed polymer device. In other words, additional

absorption does not translate into additional photovoltaic device performance. These results are not surprising; photovoltaic devices employing blended donors have produced even worse performances under many circumstances. Results from other lowbandgap polymer PBDTT-SeDPP and RR-P3HT ternary BHJ solar cells are summarized in Supplementary Fig. 2, and the device performances of these two unsuccessful ternary systems are summarized in Supplementary Table 1.

Our strategy to improve the performance of multiple-polymer systems is to optimize the compatibility of the individual donor materials, allowing them to work more like independent cells. The molecular compatibility of two or more polymers can be intuitively expected to correlate with various structural similarities. In the pool of available model materials, PBDTTT-C, PBDTT-DPP, PTB7 and PBDTT-SeDPP all have the rigid planar BDT unit in their backbone. Face-on with respect to the substrate is the preferred orientation for these polymers in deposited active layers.

Taking both molecular compatibility and absorption characteristics into consideration, a ternary blending system was studied with PBDTTT-C:PBDTT-DPP as donors. Figure 2a,b presents device results for (PBDTTT-C:PBDTT-DPP):PC₇₀BM ternary BHJ solar cells, as well as the two binary BHJ solar cells as control devices. Individual PBDTTT-C:PC₇₀BM and PBDTT-DPP: PC₇₀BM solar cells have optimized PCE values of 6.4 and 6.2%, respectively. The EQE spectrum of the ternary BHJ device (PBDTTT-C:PBDTT-DPP = 1:1):PC₇₀BM distinctively shows the combined photoresponse of both polymer donors and, as a result, the overall photocurrent increases to 15.7 mA cm⁻², surpassing each individual binary reference system. Surprisingly, the ternary BHJ photovoltaic devices still maintain a very high FF of 65%. The optimized ternary solar cells were found to outperform the reference binary cells at certain blending ratios (Table 1), specifically 3:1 and 1:1.

Bearing in mind the knowledge obtained from the ternary BHJ photovoltaic systems discussed above, we also applied this model



Figure 2 | *J-V* and EQE characterization of (PDBTTT-C:PBDTT-DPP):PC₇₀BM and (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell systems. **a**, *J-V* curve of the (PBDTTT-C:PBDTT-DPP):PC₇₀BM ternary BHJ solar cell system measured under 1 sun conditions (100 mW cm⁻²). **b**, EQE measurement of the (PBDTTT-C:PBDTT-DPP):PC₇₀BM ternary BHJ solar cell system. **c**, *J-V* curve of the (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell system measured under 1 sun conditions (100 mW cm⁻²). **b**, EQE measurement of the (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell system. **c**, *J-V* curve of the (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell system (PBDTTT-C:PBDTT-DPP):PC₇₀BM ternary BHJ solar cell system. **c**, *J-V* curve of the (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell system. **e**, *J-V* curve of (PBDTTT-C:PBDTT-DPP):PTB7:PBDTT-SeDPP):PC₇₀BM multi-donor BHJ measured under 1 sun (100 mW cm⁻²) and dark conditions. **f**, EQE measurement of the multi-donor system.

to separate ternary blends containing PTB7 and PBDTT-SeDPP. PTB7 has a molecular structure and face-on molecular orientation that are similar to those of PBDTTT-C, and its absorption edge is blueshifted by ~10 nm, but its overall photovoltaic performance is better^{10,21}. PBDTT-SeDPP is an improved form of PBDTT-DPP, with its absorption edge redshifted by 50 nm to an onset at ~900 nm (ref. 23). These properties of PTB7 and PBDTT-SeDPP will enable us to observe the added photovoltaic effect more clearly (less absorption overlap) and are expected to give an even better ternary-blend polymer solar cell system. The ternary $(PTB7:PBDTT-SeDPP = 1:1):PC_{70}BM$ device produced an efficiency of 8.7%, which is significantly higher than for those made from its individual donor materials. For comparison, the PTB7: PC70BM binary BHJ solar cell produced 7.2% efficiency, as did the PBDTT-SeDPP:PC70BM binary BHJ solar cell (both binary cells used DCB as solvent), which gave the blended donor devices a 21% relative enhancement in PCE compared to the binary cell (Fig. 2c,d). The ternary BHJ photovoltaic outperformed each binary BHJ photovoltaic at three different polymer blending ratios (25%, 50% and 75% PBDTT-SeDPP; Table 1). The donor/acceptor (D/A) ratio in all devices was 1:2. It is worth mentioning that the performance of the ternary BHJ photovoltaic device can be expected to improve further by optimizing the D/A ratio and by changing the solvent or using a co-solvent system, because the optimized solvents for PTB7 and PBDTT-SeDPP are different, as already mentioned. As both the PBDTTT-C:PBDTT-DPP and PTB7:PBDTT-SeDPP systems appear to provide good structural compatibility and device performance, if the hypothesis is correct, it should enable the fabrication of an efficient BHJ polymer solar cell with any two blended polymers. Indeed, preliminary results show that PBDTTT-C:PBDTT-SeDPP and PBT7:PBDTT-DPP ternary BHJ solar cells also deliver reasonably good device performances

Table 1 | Device performance of the (PDBTTT-C:PBDTT-DPP):PC₇₀BM ternary BHJ solar cell system and the (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell system.

	$V_{\rm oc}$ (V)	$J_{\rm sc}$ (mA cm ⁻²)	FF (%)	PCE (%) max./avg.
PBDTTT-C:PC ₇₀ BM	0.70	14.1	64.0	6.4/6.3
(PBDTTT-C:PBDTT-DPP = 3:1):PC ₇₀ BM	0.70	15.7	65.6	7.2/7.2
(PBDTTT-C:PBDTT-DPP = 1:1):PC ₇₀ BM	0.70	15.6	64.9	7.1/7.0
(PBDTTT-C:PBDTT-DPP = 1:3):PC ₇₀ BM	0.72	13.1	65.0	6.2/6.1
PBDTT-DPP:PC ₇₀ BM	0.74	13.0	64.2	6.2/6.0
PTB7:PC ₇₀ BM	0.72	15.1	66.3	7.2/7.0
(PTB7:PBDTT-SeDPP = 3:1):PC ₇₀ BM	0.69	16.2	70.0	7.8/7.7
(PTB7:PBDTT-SeDPP = 1:1):PC ₇₀ BM	0.69	18.7	67.4	8.7/8.5
(PTB7:PBDTT-SeDPP = 1:3):PC ₇₀ BM	0.69	17.9	62.4	7.7/7.7
PBDTT-SeDPP:PC ₇₀ BM	0.68	16.9	62.9	7.2/7.1
(PBDTTT-C:PBDTT-DPP:PTB7:PBDTT-SeDPP = 1:1:1:1):PC ₇₀ BM	0.70	17.3	64.6	7.8/7.6

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Figure 3 | Photo-CELIV measurements of (PDBTTT-C:PBDTT-DPP):PC₇₀BM and (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell systems. **a-f**, Photo-CELIV transients of PBDTTT-C:PC₇₀BM (**a**), PBDTT-DPP:PC₇₀BM (**b**), (PBDTTT-C:PBDTT-DPP):PC₇₀BM (**c**), PTB7:PC₇₀BM (**d**), PBDTT-SeDPP: PC₇₀BM (**e**) and (PTB7:PBDTT-SeDPP):PC₇₀BM (**f**) with different applied electric fields. All the ternary BHJ devices have the same blending ratio of 1:1.

(Supplementary Figs 3 and 4 and Supplementary Tables 2 and 3). Furthermore, a four-donor BHJ solar cell presents a very reasonable performance of 7.8% efficiency, with EQE values close to those of the constituent polymers (Fig. 2e,f). These results conceptually indicate that mixing two or even more donor materials into one BHJ is possible, as long as they exhibit sufficient structural compatibility.

Clearly, the dramatically different results for different dualpolymer BHJ systems suggest that structurally compatible polymers can coexist efficiently, while using structurally incompatible polymers (such as P3HT and PBDTT-DPP or PBDTT-SeDPP) appears to have the opposite effect, ultimately causing severe reductions in device performance. To better understand the working mechanism as well as the different photovoltaic device performances in different ternary BHJ systems, we applied transient techniques to characterize the charge transport property and recombination dynamics.

Charge transport is critical to organic photovoltaic device performance, especially in polymer solar cells with multiple donors. Unfavourable interactions between different polymers within the active layer can easily inhibit charge transport capabilities and hence limit device efficiency. Figure 3 shows the electric-fielddependent 'charge carrier extraction in a linearly increasing voltage' (CELIV) characteristics of the binary system and its corresponding ternary systems. The effective charge carrier mobility of the organic film with moderate conductivity can be estimated based on equation $(1)^{30,31}$:

$$\mu = \frac{2d^2}{3At_{\max}^2 \left[1 + 0.36\frac{\Delta j}{j(0)}\right]} \quad \text{if } \Delta j \le j(0) \tag{1}$$

where μ is the mobility, *d* is the thickness of the BHJ active layer, t_{max} is the time when the extracted current reaches its maximum value, *A*

is the slope of the extraction voltage ramp, j_0 is the dark capacitive current, and Δj is the transient current peak height (Supplementary Fig. 5).

The effective mobility value for the charge carriers in the (PBDTTT-C:PBDTT-DPP = 1:1):PC₇₀BM ternary system was 9.6×10^{-5} cm² V⁻¹ s⁻¹, which is comparable to the mobility for the PBDTT-DPP:PC₇₀BM device (9.7×10^{-5} cm² V⁻¹ s⁻¹) and even slightly higher than the other binary reference PBDTTT-C:PC₇₀BM device (4.0×10^{-5} cm² V⁻¹ s⁻¹). Another compatible ternary BHJ solar cell system, the (PTB7:PBDTT-SeDPP = 1:1):PC₇₀BM ternary system, has an effective carrier mobility of 6.5×10^{-5} cm² V⁻¹ s⁻¹, which is comparable to its corresponding binary systems with the PTB7:PC₇₀BM device (5.4×10^{-5} cm² V⁻¹ s⁻¹) and the PBDTT-SeDPP:PC₇₀BM device (9.2×10^{-5} cm² V⁻¹ s⁻¹). This indicates that the transport property within the structurally compatible ternary BHJ solar cell is not interrupted, even if it is not enhanced.

On the other hand, in devices made from the incompatible ternary BHJ system containing P3HT and PBDTT-DPP or PBDTT-SeDPP, a very different CELIV pattern is observed (Fig. 4). Both (P3HT:PBDTT-DPP):PC70BM and (P3HT:PBDTT-SeDPP):PC70BM ternary systems showed a much broader current transient peak, suggesting that charge transport inside those BHJs is much more dispersive. The t_{max} values of these unfavourable ternary BHJ solar cells were larger, so the effective carrier mobility was at least one order lower than in the corresponding binary references. The electric-field-dependent carrier mobility was also studied by varying the highest extraction voltage. As seen in Fig. 4f, the carrier mobility of incompatible ternary BHJ devices incorporated with P3HT and low-bandgap polymers is one order lower than in compatible ternary BHJ devices. They also exhibit a stronger positive field dependence, which usually indicates the electronic transport is more disordered. The dramatically different charge transport properties within different ternary BHJ solar cell systems explain the different FF values observed for these devices.

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Figure 4 | Photo-CELIV measurements of (P3HT:PBDTT-DPP):PC₇₀BM and (P3HT:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell systems. a-e, Photo-CELIV transients of P3HT:PC₇₀BM (**a**), PBDTT-DPP:PC₇₀BM (**b**), (P3HT:PBDTT-DPP):PC₇₀BM (**c**), PBDTT-SeDPP:PC₇₀BM (**d**) and (P3HT: PBDTT-SeDPP):PC₇₀BM (**e**) with different applied electric fields. All ternary BHJ devices have the same blending ratio of 1:1. **f**, Electric field-dependent charge carrier mobility of compatible and incompatible ternary BHJ solar cell systems. The straight lines are linear fits to the data.

The charge transport study suggests that more electronic traps arise if incompatible polymers are blended; generally, these uncomplementary traps might also provide recombination centres, and the open-circuit voltage will be limited if the recombination loss is severe enough. The open-circuit voltage describes the energetic transfer process from exciton generation to free carrier collection and it is of particular interest for ternary BHJ solar cells^{32,33}. It is known that $V_{\rm oc}$ is determined by the effective bandgap of the donor/acceptor blends with the recombination loss subtracted^{34,35}. For a conventional binary BHJ, the effective bandgap might be defined simply as the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor³⁴; however, that is no longer practical for ternary or multiple-compound systems. A better way to define it is through its equivalent charge transfer state, which sets the upper limit of V_{oc} . The tunable charge transfer state is observed in some of the ternary BHJ solar cell systems³⁶. In our case we also find that the charge transfer state of the (PBTDDD-C:PBDTT-DPP):PC70BM and (PTB7:PBDTT-SeDPP):PC70BM ternary systems lies roughly between those of the relative binary systems, but is slightly closer to the one with the lower charge transfer state, as measured by the highly sensitive photo-spectral response (PSR) (Supplementary Fig. 6). The difference in V_{oc} correlates well with the measured charge transfer state, which is a hint that the recombination losses within such systems are around the same level. The recombination dynamics were directly investigated by the transient photovoltage (TPV) technique (Supplementary Fig. 7) under 1 sun light bias. The solar cell is considered as working in the open-circuit condition (connected with a $1 M\Omega$ resistor), so the TPV decay describes the recombination of photo-induced carriers³⁷. Supplementary Fig. 7a,b suggests that the carrier lifetimes of the compatible ternary BHJ solar cells are not reduced compared with their corresponding binary systems, if not increased. On the other hand, the carrier lifetimes of poorly performing ternary systems containing P3HT and PBDTT-DPP or PBDTT-SeDPP are much lower than that in the P3HT:PC₇₀BM device and are close to or lower than the lowbandgap polymer:PC₇₀BM devices. It is worth mentioning that it is not only the carrier lifetime value itself that determines the recombination rate; the open-circuit charge carrier density also matters, and can be determined by charge extraction experiments^{38,39}. To summarize, V_{oc} can be maintained well if compatible polymers are mixed, because negligible additional recombination is introduced.

To correlate the electronic properties of the ternary blending and photovoltaic device performance with structural information and to understand the physical origin on a molecular level, grazing incidence wide angle X-ray scattering (GIWAXS) was performed. Two-dimensional GIWAXS patterns for each individual polymer and their blends are shown in Fig. 5. All thin-film samples were measured on a Si substrate (with a naturally formed SiO₂ surface) pre-coated with 30 nm PEDOT:PSS. Distinct out-of-plane peaks appear in the PBDTTT-C, PBDTT-DPP, PTB7 and PBDTT-SeDPP films (with $q_z = 1.57 \pm 0.06$ Å, 1.60 ± 0.06 Å⁻¹, 1.61 ± 0.06 Å⁻¹ and $1.60 \pm 0.06 \text{ Å}^{-1}$, respectively); these are associated with the $\pi - \pi$ stacking distance of 4.0 \pm 0.2 Å. This indicates that the π - π stacking direction is perpendicular to the substrate in such films, and thus they prefer a face-on orientation. When PBDTTT-C and PBDTT-DPP are blended together, this π - π stacking peak still appears in the two-dimensional GIWAXS pattern with $q_z = 1.58 \pm 0.06 \text{ Å}^{-1}$, which

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Figure 5 | GIWAXS patterns and RSoXS profiles. a-i, GIWAXS patterns for PBDTTT-C (**a**), PBDTTT-C:PBDTT-DPP blend (**b**), PBDTT-DPP (**c**), P3HT: PBDTT-DPP blend (**d**), P3HT (**e**), PTB7 (**f**), PTB7:PBDTT-SeDPP blend (**g**), PBDTT-SeDPP (**h**), P3HT:PBDTT-SeDPP blend (**i**). Each colour scale is a measure of intensity, in units of counts. **j**, RSoXS profiles (open symbols) and calculated *I*(*q*) (solid lines). **k**, Corresponding *P*(*r*) of (PBDTTT-C:PBDTT-DPP):PC₇₀BM (red), (PTB7:PBDTT-SeDPP):PC₇₀BM (blue), (P3HT:PBDTT-DPP):PC₇₀BM (green) and (P3HT:PBDTT-SeDPP):PC₇₀BM (orange).

suggests that the preferred molecular orientation with respect to the substrate remains unchanged in the blended film.

The π - π stacking coherence length can also be estimated using the full-width at half-maximum (FWHM) of the scattering peaks based on the Scherrer equation^{40,41}. We found that the coherence lengths along the π - π stacking direction for PBDTTT-C, PBDTTT-C:PBDTT-DPP blend and PBDTT-DPP are 15, 19 and 15 Å, respectively, which correspond to roughly three to four stacked molecules in pristine polymer films, slightly increasing to approximately four to five stacked molecules in the blended film. These results indicate a general retention of π - π coherence length $(L_{\pi-\pi})$ after the two face-on polymers are mixed, which is a promising sign of their ability to form compact films without one polymer disrupting the morphology and stacking structure of the other polymer. Similarly, the distinctive π - π stacking peak is also retained in the PBT7:PBDTT-SeDPP blended film, and the π - π coherence length $(L_{\pi-\pi})$ is 17 Å, comparable to that for pristine PTB7 (18 Å) and pristine PBDTT-SeDPP (17 Å).

The π - π stacking peaks in pure P3HT films are shown both in-plane and out-of-plane, but more manifestly in the in-plane axis with $q_y = 1.61 \pm 0.01$ Å⁻¹, indicating a stronger preference for the edge-on orientation. Three distinct peaks arising from the (100), (200) and (300) Bragg diffraction peaks corresponding to periodic P3HT lamellae in the out-of-plane direction were also observed, as have been reported in previous structural studies of P3HT films¹⁷. Unfortunately, on blending the PBDTT-DPP with P3HT, no scattering peaks corresponding to π - π stacking of either polymer (particularly PBDTT-DPP) could be observed in the out-of-plane direction, suggesting that ordered π - π molecular packing along the vertical direction is significantly suppressed in mixtures of P3HT and PBDTT-DPP. It is generally believed that the face-on orientation is more favourable for photovoltaic devices because of its vertical charge transportation channel. This disrupted molecular ordering along the vertical direction inevitably impedes charge transportation in the photovoltaic device. Due to the strong crystallinity of P3HT, the in-plane π - π stacking peak is still present in the blended film, but the π - π stacking coherence length $(L_{\pi-\pi})$ is reduced from 61 to 50 Å, corresponding to the number of π - π stacked molecules being reduced from ~15 to ~12, which implies that molecular ordering in the in-plane direction is also interrupted. The GIWAXS pattern for the P3HT and PBDTT-SeDPP blend demonstrates a similar trend. GIWAXS scanning curves along each direction are provided in Supplementary Figs 8 and 9. This measurement evidently tells us that molecular ordering is well maintained in a compatible polymer mixture, but is greatly disturbed by incompatible polymer blending. The molecular disorder arising from the mixing of incompatible polymers is very likely one of the key physical origins of electronic traps and recombination sites, and hence limits the photovoltaic performance of multiple-donor solar cells. The non-conjugated polymer side chain is largely insulating, and the conjugated backbone is conductive. When two polymers with different molecular orientation are mixed, as in the P3HT:PBDTT-DPP blended system, we propose that the non-conductive side chain of one polymer is likely to be

close to the conductive conjugated backbone of the other polymer. This type of unfavourable molecular pattern produces 'morphological traps', reduces the crystalline length, disrupts long-range charge transport and lowers the charge carrier mobility of the blended film. The proposed scenario of local molecular disordering is illustrated in Supplementary Fig. 10.

Besides molecular crystallinity, another important morphological factor that will determine photovoltaic performance is how these localized molecular crystals and aggregates form phase-separated domains in the BHJ. Figure 5 presents resonant soft X-ray scattering (RSoXS) profiles (open symbols), calculated scattering intensities I(q) (solid lines) and their corresponding pair distance distribution functions (PDDFs) P(r) of compatible and incompatible ternary BHJ films. (PBDTTT-C:PBDTT-DPP):PC₇₀BM, (P3HT:PBDTT-DPP):PC₇₀BM and (P3HT:PBDTT-SeDPP): PC70BM form similar domain structures at the length scales of hundreds of nanometres. As indicated by the zero crossing of P(r), (P3HT:PBDTT-DPP):PC₇₀BM and (P3HT:PBDTT-SeDPP): PC₇₀BM exhibit much larger domain sizes than (PBDTTT-C: PBDTT-DPP):PC70BM, which correlates with their unsatisfactory device performance, especially their low J_{sc} . Interestingly, the best performing (PTB7:PBDTT-SeDPP):PC70BM ternary BHJ device shows hierarchical nanomorphologies at multiple length scales, consistent with previous observations in PTB7:PC70BM40,42. A kink of P(r) at the length scales of tens of nanometres indicates that the fine domains are even smaller than those of the other three blended systems. These compositionally heterogeneous small domain regions exist inside phase-separated domains on the scale of hundreds of nanometres. It has been proposed that these hierarchical nanomorphologies are related to significantly enhanced exciton dissociation, and consequently contribute to the photocurrent⁴⁰. The retention of such nanostructural characteristics at multiple length scales not only explains the high efficiency of the (PTB7:PBDTT-SeDPP):PC70BM device, but also demonstrates that the sophisticated nanomorphology determining superior device performance can be well maintained in compatible ternary BHJ systems.

The underlying working mechanism for the ternary BHJ solar cell is complicated and varies with particular blending system. There are several possibilities to describe how the blending donor materials interact with one another: (1) the low-bandgap donor could be an near-infrared (NIR)-sensitizer (back hole transfer from a low-bandgap sensitizer); (2) exciton energy transfers from a wide-bandgap donor to a low-bandgap donor; and (3) the different donors work separately¹⁸. All three possible working principles could dominate or coexist in one particular ternary system. In the successful ternary systems studied here, the HOMOs of the blending materials are close to each other, so mechanism (1) is not likely to be dominant. Given that the photoluminescence spectra are approximately the average of the two materials (Supplementary Fig. 11), the exciton energy transfer process is excluded. The ternary BHJ device is believed to work like two parallel connected devices. The nanomorphology of each polymer matters, as both contribute to the hole transportation pathway. In incompatible polymer blending the exciton energy transfer from P3HT to the low-bandgap polymer is believed not to dominate, as indicated by the fact that the photoluminescence of P3HT is not effectively quenched by adding lowbandgap donors (Supplementary Fig. 11). Due to the relatively bigger difference in HOMO level in such a system, it is possible that the low-bandgap polymer works as an IR-sensitizer and transfers the hole to the P3HT, just as in the working mechanism in the P3HT and Si-PCPDTBT ternary system⁴³. In such a case, hole transportation is mainly determined by the morphology of the P3HT, which is interrupted by blending with incompatible low-bandgap polymers. It is also likely that mechanisms (1) and (3) coexist, so both P3HT and the low-bandgap polymers contribute to hole conduction. The nanomorphologies of both P3HT and the low-bandgap polymer are disrupted in the blended system, which provides an explanation for the hindered charge transportation and lower device efficiency. However, an alternative explanation might be that the relatively bigger HOMO level difference in P3HT and the low-bandgap polymers induces energetic disorder, which impedes charge transportation. Although it has not been confirmed that having similar HOMOs is a prerequisite for a successful ternary BHJ solar cell, ensuring only a small HOMO offset does not necessarily lead to success. Preliminary results show that a ternary BHJ consisting of PBDTTT-C (HOMO of 5.08 eV) and Si-PCPDTBT (5.16 eV), which have a HOMO offset similar to that in our successful ternary BHJ, does not deliver promising device performance (Supplementary Table 4). The effect of the HOMO level offset in ternary or multi-donor BHJ devices is definitely worth further investigation, as it plays a significant role in determining $V_{\rm oc}$ and energetic disorder.

Taken together, the GIWAXS and RSoXS results explain, on a molecular and domain scale, the dramatically different electronic and photovoltaic device performances of the two ternary BHJ systems. The blending of structurally compatible polymers (with an identical BDT unit) does not introduce significant interference into their molecular stacking preferences, and even the crystallite size and domain structure are retained. Accordingly, the electronic properties of the polymers are preserved in the ternary blends; two different molecules can coexist in harmony and contribute to an improved photovoltaic performance by broadening the absorption range. With this in mind, we can infer that molecules with complementary absorption ranges and good structural compatibility (similar crystallinity and molecular orientation) are potential candidates for the fabrication of high-performance ternary BHJ solar cells. Structural compatibility may also be linked to polymers having similar molecular groups, such as the shared BDT unit in the backbones of PBDTTT-C and PBDTT-DPP.

In summary, we report the structural, electronic and photovoltaic characteristics of several ternary BHJ solar cell systems. Two successful ternary BHJ solar cells have been demonstrated, and the best devices achieved 8.7% PCE. By comparing successful and unsuccessful multiple-donor systems, a relationship between device performance and the molecular structure of the donor materials has been established. We conclude that structural compatibility is the key factor for achieving high performance in multipledonor BHJ polymer solar cells. Indications of compatibility between polymers include preferred molecular orientation, crystallite size and domain structure, among others. This work not only proves the feasibility of producing highly efficient BHJ polymer solar cells that incorporate more than one donor material, but also provides guidelines for matching existing materials and designing new ones specifically to achieve high-performance OPVs.

Methods

Materials. P3HT was purchased from Rieke Metals, $PC_{70}BM$ from Nano-C, PTB7 from 1-Material, and PBDTTT-C from Solarmer Materials; all were used as received without further purification. PBDTT-DPP and PBDTT-SeDPP were synthesized in house according to recipes reported in previous papers^{19,23}. The polymers used in this project were all taken from the same batch in order to ensure a fair comparison between experimental and control devices.

Device fabrication and measurement. Photovoltaic devices were fabricated on indium tin oxide (ITO)-coated glass substrates that served as the anode. The ITO substrates were ultrasonically cleaned in detergent, deionized water, acetone and isopropanol. A layer of 30 nm PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly (styrene sulphonate); Baytron P VPAI 4083) was spin-coated onto the ITO substrate and dried in air at 120°C for 10 min. Polymer/PC₇₀BM or polymer blend/PC₇₀BM were dissolved in 1,2-dichlorobenzene (O-DCB) and spin-coated on top of the PEDOT layer. Finally, the Ca/Al cathode (100 nm) was vacuum-evaporated onto the annealed photoactive layer. The reference P3HT:PC70BM solar cells were spin-coated in the literature⁹, to give a thickness of ~210 nm. For both the (PBDTTT-C: PBDTT-DPP):PC₇₀BM and (PTB7:PBDTT-SeDPP):PC₇₀BM ternary BHJ solar cell

systems, the D/A ratio was kept at 1:2 and each was spin-cast from (DCB + 3% 1,8-diiodoctane (DIO)) solutions. The optimized thicknesses for PBDTTT-C: PC₇₀BM, (PBDTTT-C:PBDTT-DPP = 1:1):PC₇₀BM and PBDTT-DPP:PC₇₀BM solar cells were 100, 120 and 105 nm, respectively. In the (PTB7:PBDTT-SeDPP): PC70BM ternary BHJ solar cell system, the optimized thicknesses for PTB7:PC70BM, (PTB7:PBDTT-SeDPP = 1:1):PC₇₀BM and PBDTT-DPP:PC₇₀BM solar cells were 95, 115 and 100 nm, respectively. For the four-donor BHJ solar cell, the active layer was spin-cast from a combined solution of (PBDTTT-C:PBDTT-DPP = 1:1): $PC_{70}BM$ and (PTB7:PBDTT-SeDPP = 1:1):PC_{70}BM with a 1:1 volume ratio, so that the D/A ratio was 1:2, to give a device thickness of ~120 nm. The effective area of the devices was 0.1 cm². Current-voltage (J-V) measurements of the photovoltaic devices were conducted using a Keithley 236 source-measure unit. A xenon lamp with an AM 1.5G filter (NEWPORT) was used to simulate 1 sun conditions and the light intensity at the sample was 100 mW cm⁻², calibrated with a mono-Si photodiode with KG-5 colour filter. The reference diode was traceable to NREL certification. EQE measurements were conducted with an integrated system (QE-R3018) from EnliTech.

Photo-CELIV measurements. Photo-CELIV measurements were used to study the charge transportation property in single- and multiple-donor BHJ solar cells. A 590 nm dye (Rhodamine Chloride 590) laser-pumped by a nitrogen laser (LSI VSL-337ND-S) was used as the excitation source, with pulse energy and pulse width values of $0.03 \ \mu$ J cm⁻² and 4 ns, respectively. A triangular voltage pulse was applied by a function generator (Tektronix AFG 3532). The current transient was recorded using a digital oscilloscope (Tektronix DPO 4104). An offset voltage was applied to all measurements to compensate for the internal electric field. The field-dependent mobility was measured by modulating the highest extraction voltage. The effective electric field was determined according to E = At/d, where *t* is the time that the current transient drops back to the displacement current j_0 , which means that charge extraction is completed. CELIV is not the best method with which to determine the field-dependent mobility accurately, because the electric field is varied during measurements. Here, we focused only on a relative comparison of the field dependence.

TPV measurements. A 590 nm dye (Rhodamine Chloride 590) laser pumped by a nitrogen laser (LSI VSL-337ND-S) was used as the excitation source, with pulse energy and pulse width values of 0.03 μ J cm⁻² and 4 ns, respectively. The measurement was conducted under 1 sun conditions by illuminating the device with a white light-emitting diode. The input impedance of the oscilloscope (Tektronix DPO 4104) was 1 MΩ, and the solar cell device was considered as working in the open-circuit condition. The charge carrier could not be extracted, but was recombined. Accordingly, the transient decay represented the charge carrier lifetime.

High-sensitivity PSR measurement. The experimental set-up was similar to the setup for EQE measurements, but with much higher sensitivity. The incident light was modulated with an optical chopper at 171 Hz and the photocurrent was first amplified using a 100 k Ω resistor and captured by a lock-in amplifier (Stanford Research SR830). The photocurrent could drop by approximately six orders of magnitude before reaching the noise level.

GIWAXS. GIWAXS measurements were performed at the 8ID-E beamline at the Advanced Photon Source (APS), Argonne National Laboratory, using X-rays with a wavelength of $\lambda = 1.6868$ Å and a beam size of ~200 µm (horizontal) × 20 µm (vertical). A two-dimensional PILATUS 1M-F detector was used to capture the scattering patterns and was located 208.7 mm from the samples. All samples were prepared on PEDOT:PSS-modified Si substrates to emulate the fabrication condition for OPV devices. Typical GIWAXS patterns were taken at an incidence angle of 0.20°, above the critical angles for polymer:PC₇₀BM blends and below the critical angle of the Si substrate.

RSoXS. RSoXS transmission measurements were achieved at beamline 11.0.1.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. RSoXS measurements were taken with an X-ray photon energy of 284.2 eV to obtain the best contrast and sensitivity. Samples for RSoXS measurements were first prepared on a PEDOT:PSS-modified Si substrate under the same conditions as those used for fabrication of OPV devices and then transferred to a 1.5 mm × 1.5 mm, 100-nm-thick Si₃N₄ membrane supported by a 5 mm × 5 mm, 200-µm-thick Si frame (Norcada). Calculations of RSoXS intensities, I(q), and PDDFs, P(r), were performed using the generalized indirect Fourier transformation approach^{44,45} through the GIFT software program in the PCG software package.

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Author contributions

Y.(M.)Y., G.L. and Y.Y. conceived and developed the ideas. Y.(M.)Y. designed the experiments and performed device fabrication, electrical characterization (CELIV, TPV and highly sensitive PSR) and data analysis. W.C. performed GIWAXS and RSoXS measurements and analysed the data. L.D. and W.-H.C. synthesized and provided the low-bandgap polymers of PBDTT-DPP and PBDTT-SDPP. S.D. assisted with highly sensitive PSR measurements. Y.(M.)Y., G.L. and Y.Y. wrote the manuscript. B.B. and W.C. contributed to revision of the manuscript. The projects were supervised by Y.Y. and G.L.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to G.L. and Y.Y.

Competing financial interests

The authors declare no competing financial interests.