1. Introduction

Organic solar cells (OSCs) show increasing potential, recently achieving over 16% power conversion efficiencies (PCEs) for single-junction devices. OSCs are a versatile technology due to their solution processability, compatibility with low cost roll-to-roll production, flexibility, lightweight, and aesthetically tunable properties, which makes them appealing when compared to their inorganic counterparts.

Different strategies are being followed in order to improve the initially low PCE of OSCs, such as the synthesis of novel materials including low bandgap donor polymers and non-fullerene acceptors (NFAs); deeper understanding and control of the active layer morphology through side-chain engineering; improved hole- and electron-extracting interlayers; multi-junction devices (tandem structures), etc. Among them, the ternary bulk heterojunction (BHJ) has emerged as an efficient route to improve the photovoltaic performance of single-junction OSCs. In a ternary OSC, three materials are used in the active layer of the OSC instead of the original BHJ binary blend (donor:acceptor, D:A). In most cases, the ternary consists of either one donor and two acceptors (D:A 1:A 2) or two donors and one acceptor (D 1:D 2:A). Ternary blends often result in improved performance of one or more of the photovoltaic parameters in the OSC compared to the corresponding binaries, thus increasing the final PCE.

While a full understanding of ternaries is yet to be developed, a number of mechanisms have been identified to contribute to this improvement. These include the increase in light harvesting by broadening of the absorption spectrum through the use of materials with complementary absorption spectra; a more efficient exciton dissociation and better charge carrier transport due to the formation of cascade energy levels; improved photocurrent due to tailored phase separation landscape and improved stability by lock-in microstructure; and enhanced open circuit voltage due to an effective alloying effect.

Indeed, some ternary OSCs are among the best performing devices reported to date. The performance of ternary OSCs depends greatly on several parameters that must be taken into account and optimized. The choice of donor and acceptor materials forming the active layer, its blending ratio and the final film thickness are just a few, and they require careful optimization to achieve the most favorable nanomorphology in the ternary BHJ layer. The composition ratio affects the phase separation and crystallinity of the materials, ultimately modifying the electrical transport properties and the final PCE of the OSC.

The most conventional optimization protocol in ternary OSCs relies on the fabrication of tens of samples, which is extremely tedious and resources-consuming. The composition...
phase space is 2D, exponentially increasing the number of samples needed for a comprehensive study of the ternary system compared to binaries.[18] As a result, the vast majority of research done in ternary OSCs only partially explores the ternary composition phase space. Indeed, the most common strategy consists of keeping the total D:A ratio fixed (typically at 1:1), while varying the relative composition of the two materials that have the same electronic character, i.e., D_{1}(A_{0}, A_{0}) or (D_{1}, D_{2}):A_{0}.[7,9,17] Nevertheless, there is no evidence, nor a fundamental principle, suggesting that the optimum blending ratio should be found along the 1:1 D:A composition trajectory.[12] In fact, many binary systems characterized by unbalanced transport or optical properties show optimum compositions far from the 1:1 ratio. Similar arguments could also be applicable to ternaries.[9,12,15] Moreover, since the optimization process typically performed is very limited, the absolute optimum performance might still remain unknown, which opens the possibility for an even greater improvement than what was initially thought and reported. There may even be more than one maximum in the composition phase space. The challenge, then, becomes finding a methodology that enables exploring the ternary phase space in an efficient fashion.

For the simpler case of BHJ binary blends, the optimum composition ratio lies along a 1D line, i.e., somewhere in between 1:0 and 0:1 D:A ratios. A discrete and limited exploration of the optimum blending ratio in a single binary blend requires the fabrication of several devices; the efficiency optimization requires simultaneously optimizing the active layer thickness for each composition, thus rapidly scaling up the number of samples required for evaluating a binary system. For this kind of complex multiparametric problems, we have recently proposed alternative approaches based on the high-throughput screening of BHJ binary systems and bilayered heterojunction devices.[19,20] The main concept of these methodologies is the fabrication of samples with gradients in the parameters of interest, and then imaging the performance over the gradient to locate the optimum conditions.

Inspired by the success of that work, here we present a novel methodology to perform high-throughput processing and evaluation of the performance in ternary BHJ OSCs. The methodology minimizes the use of samples and resources by fabricating large-area devices with lateral composition gradients which are equivalent to a large library of homogeneous samples. The fabrication of the samples is based on a layer-by-layer or sequential deposition of the active layer materials by means of blade coating.[21,22] All three materials are dissolved in individual solutions without the need for premixing them and deposited sequentially along different coating directions and with effective thickness gradients. The realization of orthogonal and lateral thickness gradients allows the creation of a broad library of blending ratios in a single sample, covering different regions of the ternary blend diagram. These samples are then hyperspectrally imaged by using 1) Raman imaging, which serves to quantify the local composition of the blend; 2) photoluminescence (PL) imaging, to assess the degree of mixing and infer potential \( V_{oc} \) changes; 3) absorption spectra imaging, which can be connected to the local photocurrent; 4) light beam induced current (LBIC), using monochromatic laser beams to extract the local photocurrent and being able to address the different materials separately, at least in part, by changing the excitation wavelength when the materials exhibit non-overlapping absorption spectra; and 5) white light beam induced current (WhiteBIC) to correlate the local photocurrent with a more realistic performance in Sun operating conditions. The combination of these large datasets, which are acquired colocoly using the same setup, reveals a complicated performance landscape including, in some cases, the emergence of more than one photocurrent maximum. We apply this machinery to three different D:A,\(_1\):A,\(_2\) ternary blends, namely, PBD(T)-T:ITIC:PC\(_{70}\)BM; PTB7-Th:ITIC:PC\(_{70}\)BM; and P3HT-O-IDFBR-O-IDTBR. Our results indicate that the usual strategies followed to optimize blending ratios in ternary blends, such as keeping fixed the total D:A ratio in the ternary blend, might lead to incomplete conclusions with underestimated performances. This finding is highly relevant for the ternary BHJ technology as it suggests that PCEs can be boosted even further by fully exploring the composition landscape.

2. Optical Characterization: Raman Imaging of Ternary BHJ Blends

2.1. General Considerations and Requirements

Currently, the realization of panchromatic active layers is feasible given the low bandgap nature of conjugated polymers (Figure 1c) and the bandgap tuning capability of conjugated small molecules (Figure 1d), specially the new generation of NFAs such as ITIC. Therefore, we have decided to investigate three different D:A\(_1\):A,\(_2\) blends in the active layer: PTB7-Th:ITIC:PC\(_{70}\)BM; PBD(T)-T:ITIC:PC\(_{70}\)BM; and P3HT-O-IDFBR-O-IDTBR. The first two combinations are expected to maximize the absorption as they combine a low bandgap polymer (PTB7-Th or PBD(T)-T) with the low bandgap and highly absorbing ITIC, together with the UV-absorbing PC\(_{70}\)BM which could help in harvesting shorter wavelength photons while improving the morphology of the film.[23,24] On the other hand, the ternary blend P3HT-O-IDFBR-O-IDTBR represents a paradigmatic example of complementary absorption that has recently been demonstrated to yield PCEs as high as 7.7%, which is a promising value given the low cost associated to the mass production of such active layer materials.[17]

The determination of the local composition of inhomogeneous blend films by means of Raman spectroscopy underpins our high-throughput methodology.[19,20,25] This technique enables the use of gradients produced from solution with moderate spatial control. It imposes certain restrictions, however, in the materials to be tested, which we need to pre-evaluate for the selected ternaries. First, all materials should be clearly distinguishable in terms of their vibrational fingerprint. In this sense, the heterogeneity of the conjugated backbones in organic semiconductors translates into peak-rich and characteristic vibrational spectra, mainly in the spectral window associated to C=C and C=C stretching modes (≈1200–1600 cm\(^{-1}\)).[26] Figure 1a depicts the vibrational Raman spectra of three different donor materials, namely PBD(T)-T (aka PCE12), PTB7-Th (aka PCE10), and the workhorse p-type polymer RR-P3HT. Figure 1b illustrates the Raman vibrational fingerprint of four different conjugated small molecules used as electron transporting materials: a fullerene acceptor, PC\(_{70}\)BM; and three
NFAs, ITIC, O-IDTBR, and O-IDFBR. A thorough inspection of this vibrational library indicates that all possible ternary combinations should be, in principle, clearly identified. The Raman fingerprinting capability does not, hence, represent an important restriction in this sense (see also Ref. [25]).

Additionally, a successful analysis of ternary blend films requires the Raman cross-section of the materials to be similar enough to properly deconvolute the spectra and enable an accurate quantification of the composition of the film; otherwise, the large Raman intensity ratio between dissimilar materials might hinder or even impede a proper deconvolution.[20,25] Table 1 summarizes our experimentally deduced Raman cross-section for the seven materials employed, a determination that requires previous knowledge of the complex refractive index of each material (see Figure 1) and the measurement of the thickness-dependent Raman signal using a sample with a thickness wedge.[25] Following our previous accuracy estimates, only those blends including RR-P3HT as donor and either ITIC or PC70BM as acceptor(s) would be problematic due to its cross-section ratio being larger than 30.[25] Note that the Raman cross-sections and refractive indices only need to be measured once per material, and can be also taken from literature.

2.2. Quantification of the Volumetric Composition in Ternary Blends

We have recently demonstrated that Raman spectroscopy constitutes a powerful tool for the mapping of film features such as thickness and composition by properly deconvoluting and quantifying the scattered Raman intensity.[19,20,25] The approach applies even to active layers in working devices as the thickness and complex refractive indices of the interlayers are considered in the transfer matrix modeling. So far, the methodology has been applied to binary BHJ blends as well as evaporated bilayer OSCs.[19,20] Nevertheless, the extension to BHJ ternary blends is straightforward as the third component is added as an extra term in the corresponding scattered field intensity calculations

\[ I_{R,\text{blend}}(d, \nu, \omega) \propto \int_0^1 [E_x(x, \nu)]^2 \sum_{\nu_n} v_n \sigma_{R,n} I_{\text{ref}, n}(\omega) \]  

(1)
where \( d \) stands for the thickness of the blend film; \( \nu_i \) is the volumetric fraction of the \( i \)-th component; \( \omega \) refers to the frequency or Raman shift; and \( I_{\text{ref},i} \) represents the reference Raman vibrational fingerprint of the \( i \)-th component normalized at the intensity of the mode associated with the cross-section \( \sigma_{\text{R},i} \) (see Table 1). The transfer matrix calculation computed to get the scattered intensity term, \( |E_\text{R}(x,\nu)|^2 \), depends on both the blend film thickness and its volumetric composition. The film thickness modulates the scattered intensity, while the volumetric blending ratio is assumed to weight the complex refractive index of the film as \( \epsilon_{\text{blend}} = \sum \nu_i \epsilon_i \).

In the case of ternary blends with complementary absorption profiles the Raman scattered intensity at 488 nm excitation sharply oscillates as a function of the active layer thickness, reaching the absolute maximum at \( \approx 60-70 \) nm of film thickness; this is a consequence of the large oscillator strength exhibited throughout the visible regime in this sort of blends and also due to the interference enhancement of the metallic back electrode encountered in the functional device.\(^{25}\) This fact constrains the accessible range and reliability of thickness values characterized by means of Raman spectroscopy to a window that is usually far from the optimum in OSCs (\( \approx 100-110 \) nm). Furthermore, the estimation of the complex refractive index in ternary blends as a weighted linear combination of the pristine indices might be too simplistic considering the morphological changes upon mixing.\(^{26}\) This could be especially problematic when blending materials with large extinction coefficients in pristine films, such as PBDB-T, ITIC, or O-IDTBR (Figure 1), thus adding extra uncertainty to the transfer matrix calculations.

On the other hand, while the optical constants are highly dependent on the environmental and surroundings of the embedded optical transition dipoles, we expect the Raman cross-sections, which respond to local vibrations of the embedded optical transition dipoles, we expect the Raman cross-sections, which respond to local vibrations of the embedded optical transition dipoles, to individual vibrations of the molecules. Therefore, an extra degree of freedom is added to improve the goodness of fit, namely, a small rigid shift of the Raman peaks, \( \delta_{\nu} \), finally yielding

\[
I_{\nu,\text{blend}}(\beta, \nu, \omega, \delta_{\nu}) \propto \beta \sum_{i=1}^{3} \nu_i \sigma_{\text{R},i} I_{\text{ref},i}(\omega + \delta_{\nu})
\]

(3)

Note that, experimentally, \( \delta_{\nu} < 0.5\% \) the value of \( \omega \). We have systematically observed that for the different samples and material combinations studied here, the model summarized in Equation (3) leads to significantly improved fits of the experimental data compared to the rigorous case in Equation (1). We show in Figure S1, Supporting Information, a comparison of these three methods in the fit of a ternary sample with gradients. Equation (3) model has the virtue of making fewer assumptions regarding the similarity of the structure in the pristine materials and their corresponding blends. Indeed, we will show below that imaging \( \delta_{\nu} \) for the vibrations corresponding to each material provides useful insights into the degree of mixing and/or purity of the structural domains. An additional analysis of the sources of uncertainty in the determination of compositions can be found in the Supporting Information.

### 3. Generation of Ternary Blend Libraries

The high-throughput screening of ternary blends requires the generation of blend composition libraries covering the largest possible area in the ternary diagram. This should be realized using the minimum number of samples (i.e., time and resources) in combination with rapid characterization techniques to be truly effective and high-throughput experimentation. We have recently demonstrated that, for binary D:A blends, it is possible to cover the entire composition range (from 1:0 to 0:1) in a single large-area solar cell by blade coating two nearby drops of the pristine solutions.\(^{19}\) The processing results in films showing lateral composition and thickness gradients when combined with accelerated blade coating. Their superior characterization by means of Raman spectroscopy mapping and LBIC yields, in a single run, the active layer parameters (thickness and composition) which maximize the photovoltaic performance. For the generation of ternary blend composition libraries, we first tried to adapt our previous experience on the generation of binary composition gradients.\(^{19}\) We explored the coating of nearby drops atop a solid dried film, which resulted in limited and localized composition ratios in the ternary diagram. We therefore, explore a number of different deposition approaches which included multiple drops and sequential deposition. Among the variety of approaches we tested, we found that the sequential (or layer-by-layer) deposition of films yielded the more complete and reproducible ternary libraries. The details of this approach are described in the following paragraphs.

Ternary blend libraries are obtained by processing the active layer as a sequential deposition of each of the pristine solutions (D, A1, and A2), one on top of the other, while using the same solvent and processing parameters (stage temperature and blade speed). Interestingly, the sequential deposition using non-orthogonal solvents does not lead to the detachment of
the underneath layers but to a vertical intermixing and gradual vertical segregation in some cases. This approach is also known as layer-by-layer deposition and has recently been demonstrated to yield an optimized vertical phase segregation in some polymer:NFA binary OSCs when the devices are processed in accordance with their vertical architecture, i.e., with the donor (acceptor) layer facing the anode (cathode).[21,28]

Our exploration regarding D:A\textsubscript{1}:A\textsubscript{2} blends indicates that the layer coating order matters to realize proper ternary active layer film libraries. The processing must start with the donor (polymer) first, followed by the acceptors (small molecules) in sequential layers. We hypothesize this requirement is related with the viscosity of the polymeric solution, which turns out to be critical when the donor is casted in second or third place. In such cases, we do not observe a significant exploration of the ternary composition diagram but the formation of either binary blends (when the polymer is deposited in second place) or even to the absence of blending (when the polymer is deposited in the last place), as evidenced from Raman scattering measurements.

The importance of viscosity is apparent for ternary combinations of the type D\textsubscript{1}:D\textsubscript{2}:A, containing two donor polymers and a small molecule acceptor. Figure S2, Supporting Information, shows the ternary phase diagram for one such sample, consisting of the P3HT:PCDTBT:PC\textsubscript{70}BM ternary. More than 80% of the composition space can be explored in a single sample by properly matching the ink viscosities and casting parameters.

Therefore, after first coating the donor polymer layer, we proceed with the sequential coating of the acceptor layers. These layers are processed by spreading the pristine solutions from collateral corners of the large aspect-ratio, 75 mm long by 25 mm wide, indium tin oxide (ITO) substrates we use as transparent conductive electrode (see Figure 2). By setting up the blade coating process to start at a sharp substrate corner we obtain a rather controllable thickness gradient driven by the variation of the wetting front width as the blade moves over the substrate. Experimentally this is an appealing approach to obtain gradients as it simply requires rotating the substrate by 45° with respect to the coating direction to get the steepest thickness gradient. Hence, by combining in a single sample the layer-by-layer deposition consisting of a homogeneous polymer film followed by two different small molecule acceptors blade coated from collateral corners, we explore a large area of the ternary composition diagram, as depicted in Figure 2a. The region explored can be tuned, at least in part (either I, II, or III in Figure 2a) depending on the thickness of the layers, which is mainly determined by the solution weight loading and the coating speed. In fact, we checked that by blade coating the first polymer layer in the form of a lateral thickness gradient (by accelerating the blade speed) we could purposely extent the range of donor loading explored in the ternary diagram (Figure 2b).

4. Ultrafast Characterization of Ternary Libraries

Figure 3 illustrates a set of the raw mapping data extracted from a single ternary sample of PTB7-Th:PC\textsubscript{70}BM:ITIC processed according to the thickness gradient method depicted in Figure 2b. In this case, a PTB7-Th thickness gradient was deposited from left ([−20, y]) coordinates in Figure 3a) to right ([25, y]); then a pristine solution of PC\textsubscript{70}BM was casted in diagonal from the top-left corner ([−20, 0]); and finally the ITIC layer was processed from the top-right corner of the sample ([25, 0]).

In order to minimize measuring time, we begin by performing a coarse (low-resolution, 45 × 25 positions) photocurrent map with white light illumination (Figure 3a) which takes less than 15 min to complete for a large area of 45 × 25 mm\textsuperscript{2}. This coarse photocurrent map is intended to quickly identify and locate the high performing areas of the device, thus the region of interest. This area is then zoomed in and imaged with higher resolution (Figure 3b) and several complementary techniques. During the acquisition of this high resolution photocurrent map, we simultaneously collect the reflectivity spectra of the full device stack (R\textsubscript{Ag}) at each position. This reflection map, after normalization by the reflectivity of the back electrode (usually silver, R\textsubscript{Ag}), yields the absorption (A) of the device as \( A = 1 - R\textsubscript{Ag}/R\textsubscript{Ag} \) at each position. Absorption maps at selected wavelengths are shown in Figure 3c–g. We then proceed with the monochromatic characterization of the device by using a 633 nm laser to measure photocurrent (Figure 3d) and at the same time PL (Figure 3e) in a single run. While less precise than electroluminescence measurements, the energy of the PL maximum can be correlated in some cases with the charge transfer energy, and thus used as a proxy for effective local \( V\textsubscript{OC} \) (Figure S3, Supporting Information).\[29\] PL quenching could also be correlated with efficient charge transfer and thus, with the degree of mixing. Finally, we colocally measure the Raman scattered spectra (which integrated intensity is depicted in Figure 3h) and the photocurrent at 488 nm excitation (Figure 3c). The selection of 488 nm as excitation wavelength in Raman scattering is related to the cross-section compatibility between materials, the fulfillment of resonant conditions and the absence of disturbing PL.

Figure 2. Sketches of the sequential blade coating deposition steps used to explore ternary blend composition diagrams for a) a homogeneous first donor layer and b) a thickness gradient as the first donor layer. The dots correspond to experimental data obtained for a RR-P3HT:O-IDFBR:O-IDTBR ternary.
backgrounds which could potentially hinder the deconvolution of the spectra. The complete set of optical characterization images includes two low resolution images, three 3D images (photocurrent with typically \(86 \times 50\) spatial points each) and three 4D images (Raman, absorption, and PL spectra \((86 \times 50)\) points \(\times 1024\) spectral points), which add up to more than 13 million experimental data points. All these measurements are performed in a row and using a single (confocal Raman) setup in less than 3 h, thus representing a paradigmatic example of high-throughput evaluation of solar cells.

The white light photocurrent maps (Figure 3a,b) are acquired using the built-in lamp in our confocal Raman scattering setup, which due to technical limitations cannot be coupled to an external illumination source, such as an AM1.5 solar simulator. Even so, the emission spectrum of the lamp spans most of the visible/NIR range (Figure S4, Supporting Information), thus we expect the corresponding photocurrent maps being qualitatively similar to what we would obtain using a dedicated light source, albeit somewhat UV and NIR poor, thus slightly underestimating the photocurrent of materials that absorb strongly on those regions. The importance of using broadband illumination instead of the more standard laser is apparent when comparing the WhiteBIC (Figure 3b) and LBIC at 488 nm (Figure 3c) and 633 nm (Figure 3d). The single-wavelength photocurrent maps clearly indicate that the maximum photocurrent is generated at a different location (i.e., a different active layer thickness and blend composition) with respect to what we observe with white light illumination. We could expect this type of behavior for systems with at least partially complementary absorptions in which all materials contribute to the photocurrent: monochromatic illumination may be indicating a region rich in a material with strong absorption at that specific wavelength, rather than the real optimum of the whole cell. This result indicates that white light should be employed in order to evaluate the performance of non-fullerene binaries and ternary devices in typical operating conditions. Furthermore, our experience suggests that the use of white light illumination focused as a large spot of \(\approx 200 \mu m\) in diameter leads to qualitatively smoother photocurrent maps, i.e., less prone to suffering spatial photocurrent fluctuations associated to scattering by defects and dust. Despite using low magnification (10X) and low numerical aperture objectives (NA 0.25), the photocurrent maps measured using monochromatic sources of light (Figure 3c,d) generally show a larger density of photocurrent spikes. This is a result of the smaller spot size (typically 10 \(\mu m\) in diameter) and more pronounced focusing ability of monochromatic light, which is then more likely to scatter at the tiny defects (aggregates, scratches, dust) encountered throughout the layered device stack and the substrate. We would like to emphasize that the photocurrent images are not the result of a hidden thickness variation, as the thickness and photocurrent maps do not seem to be correlated (Figure S5b, Supporting Information).

The acquisition of monochromatic photocurrent maps is, however, useful to identify the relative contribution of the blended components to the generation of free charge carriers. For the ternary blend studied in Figure 3, we expect the absorption spectrum being largely panchromatic due to the complementary absorption of its components, PTB7-Th:PC_{70}BM:ITIC (Figure 1).
According to their complex refractive index, at 633 nm excitation PTB7-Th and ITIC domains should be selectively contributing to the photogeneration of excitons, while at 488 nm excitation all three materials are absorbing. Also, the overall extinction is likely to be higher at 633 nm (Figure 3g) than at 488 nm (Figure 3f) excitation due to the noticeable larger oscillator strength of PTB7-Th and ITIC at 633 nm than PC70BM at 488 nm excitation. Interestingly, the 633 nm LBIC follows quite closely the ITIC composition (Figure S5, Supporting Information), which is reasonable given the very high oscillator strength of this material at these photon energies (Figure 1d). The absorption map at 633 nm shown in Figure 3g correlates well with the total volumetric fraction of PTB7-Th and ITIC obtained from the quantitative analysis of the Raman scattered intensity (Figure S5d, Supporting Information). Conversely, the spatial variations observed in Figure 3f are closely matching the measured volumetric fraction map of PC70BM in the ternary blend (Figure S5e, Supporting information). Examples of the raw absorption, PL and Raman spectra at selected loci are given in Figure S6, Supporting Information. Interestingly, and despite the larger absorption at 633 nm, we observe that both monochromatic photocurrent maps are quantitatively similar (Figure 3c,d). The fact that the maximum white light photocurrent is displaced with respect to the monochromatic photocurrent maps and absorption maps suggests that the optimum composition results from the fine balance between optical properties and electronic transport (facilitated with increasing fullerene content). This is, for instance, reflected by the fact that the optimum composition for samples before and after annealing is different (Figure S7, Supporting Information). Upon thermal annealing, a second photocurrent maximum emerges at a ratio of 0.2:0.6:0.2 (v:v:v) which is indicative of an improved film morphology motivated by the annealing process (see below). The third and markedly higher photocurrent maximum corresponds to a ratio of 0.2:0.2:0.6 (v:v:v). The first two maxima may be absorption dominated cases (ITIC exhibits high oscillator strength, see Figure 1), while the third may correspond to a ternary composition characterized by good-extraction properties. A deep minimum in performance is found for a ratio of 0.5:0.3:0.2 (v:v:v) which is observed in both samples. Interestingly, such minimum lies on the usual blending ratio scheme followed in the literature, i.e., keeping the donor loading fixed at 50%, while varying the ratio of both acceptors. We observe that the high performing areas are located in regions of low polymer loading (15–30 vol%); then, the three maxima differ in the ratio of the acceptors, being the more favorable a larger PC70BM loading in the present case. The reason for this dissimilar optimization blending ratios is likely to be related to the aforementioned optical versus transport compromise, together with a variable degree of phase separation and type of nanomorphology attained for each composition.[16]

In order to doublecheck the existence of two photocurrent maxima scenario in PTB7-Th:ITIC:PC70BM ternary blends, we have fabricated samples with fixed stoichiometry. These samples were fabricated to exhibit a thickness gradient in order to fully explore the parametric landscape. In this set of samples the donor weight fraction was kept constant at 25 wt%, while the relative acceptor loadings were varied accordingly to follow the composition trajectory that included several maxima in the ternary library (Figure 4a). The results depicted in Figure 5c (including two binaries and four ternary combinations) indicate that when looking at the top performing shell of devices an acute photocurrent drop occurs close to 0.25:0.35:0.40 (w:w:w) ternary ratio, resulting in two photocurrent maxima. Upon extraction of the corresponding volumetric loading ratios through Raman spectroscopy (Figure 5b) we observe that the location of the minimum and both maxima matches the previously found ratios (Figure 4a). Note that due to the dissimilar typical densities of polymers (1.0–1.1 g cm$^{-3}$) and small molecules (1.3–1.7 g cm$^{-3}$), there is a large shift between volumetric and weight loading ratios that has to be considered when interconverting such

5. Performance Phase Diagram in Ternary Systems

The colocal acquisition of the characterization maps illustrated in Figure 3 and Figure S5 (Supporting Information) enables the removal of their spatial dependence. Therefore, the relevant parameters can be plotted in ternary composition diagrams by matching them with the composition maps extracted by means of Raman imaging spectroscopy (Figure S5, Supporting Information). Figure 4 depicts the corresponding diagrams for two different and thermally annealed PTB7-Th:ITIC:PC70BM devices. In the two samples, acceptor layers were processed in different order to cover complementary areas of the diagram. Note that in these plots only the regions of highest performance were zoomed in and analyzed with increased spatial resolution. Figure 4a depicts the local photocurrent extracted under white light illumination over the phase diagram of the ternary. We identify up to three different photocurrent maxima on a relatively smooth landscape. The first and lower one is centered at a blending ratio of PTB7-Th:ITIC:PC70BM 0.35:0.60:0.05 (v:v:v), which matches the single maximum we observed in the same sample prior to the annealing process (Figure S7, Supporting Information). Upon thermal annealing, a second photocurrent maximum emerges at a ratio of 0.2:0.6:0.2 (v:v:v) which is indicative of an improved film morphology motivated by the annealing process (see below). The third and markedly higher photocurrent maximum corresponds to a ratio of 0.2:0.2:0.6 (v:v:v). The first two maxima may be absorption dominated cases (ITIC exhibits high oscillator strength, see Figure 1), while the third may correspond to a ternary composition characterized by good-extraction properties. A deep minimum in performance is found for a ratio of 0.5:0.3:0.2 (v:v:v) which is observed in both samples. Interestingly, such minimum lies on the usual blending ratio scheme followed in the literature, i.e., keeping the donor loading fixed at 50%, while varying the ratio of both acceptors. We observe that the high performing areas are located in regions of low polymer loading (15–30 vol%); then, the three maxima differ in the ratio of the acceptors, being the more favorable a larger PC70BM loading in the present case. The reason for this dissimilar optimization blending ratios is likely to be related to the aforementioned optical versus transport compromise, together with a variable degree of phase separation and type of nanomorphology attained for each composition.[16]
magnitudes. It is important to highlight that due to the dispersion in photocurrent induced by the active layer thickness variations (y-axis in Figure 5c) ternary libraries might lead to incomplete performance landscapes if such parameter is not fully explored. However, this limitation can be circumvented through the complementary use of active layer thickness gradients once the optimum performance ratio is identified.

This set of stoichiometrically controlled devices serves to validate the high-throughput generation of ternary libraries as in terms of photovoltaic performance it leads to the same conclusions obtained following the traditional sample-by-sample methodology, albeit with a noticeably increased statistical meaning and reduced use of resources and time. Furthermore, we have confirmed that: i) in ternary systems multiple

Figure 5. a) Optical image of a sample consisting of 24 different devices (12 per side) with the ternary PBT7-Th:ITIC:PC70BM blend as active layer. The active layer was blade-coated as a lateral thickness gradient. b) Representation of the ternary composition diagram of six different samples (24 devices each, of variable thickness and fixed stoichiometric ratios), with the highest photocurrent obtained in the sample as color scale. c) Photocurrent dispersion obtained for all wedge-like samples (keeping fixed PBT7-Th loading at 25 wt%) as a function of ITIC wt%. The black line is a guide to the eye.
photocurrent maxima are feasible; ii) the thickness exploration using gradients is sufficient to capture the essence of the problem; and iii) the error in the determination of the composition using Raman is typically of the order of 5%–10%, which is an estimation based on the dispersion observed in Figure 5b for stoichiometrically controlled devices. Further details regarding the accuracy and error estimations of the Raman methodology are provided in the Supporting Information.

To gain further insights about the extent in which the film morphology is critical for the device performance, we performed further analysis of the Raman spectra, focusing now on the shifts of the corresponding vibrational modes. Raman mode shifting in conjugated polymers constitutes a phenomenon typically observed upon blending with small molecules. Depending on their degree of miscibility, the small molecules are able to intercalate throughout the polymer domains disturbing their planarity and conjugation length while affecting the intermolecular interactions. For simplicity, we perform the Raman shift analysis by assuming that the vibrational fingerprint of each material is rigidly shifted according to a corresponding $\Delta\delta$ parameter (see Equation (3)). In the case of PTB7-Th (Figure 4b), we notice that its vibrational bands are blueshifted with respect to the reference spectra taken in pristine polymer films. Still, the shift is not as large as that observed upon degradation for the related compound PTB7,[30] thus suggesting that the observed dispersion is likely due to changes in the morphology of the film. Interestingly, the high performing areas explored in Figure 4a correlate well with large blueshifts ($\approx 3 \text{ cm}^{-1}$) in PTB7-Th, being more pronounced at high PC70BM loadings ($\approx 5 \text{ cm}^{-1}$); conversely, in the low performing areas, the Raman shift of PTB7-Th vibrational bands is, in average, close to zero. These findings suggest, on the one hand, that PTB7-Th requires a thorough intermixing with the acceptors to yield an efficient splitting of the photogenerated excitons; and, on the other hand, that the miscibility of PC70BM with PTB7-Th is larger than that of ITIC. The corresponding ternary diagrams for the Raman shift of ITIC (Figure 4c) and PC70BM (Figure 4d) do not show a significant dispersion close to the highest photocurrent maximum, thus suggesting that purer ITIC and PC70BM domains coexist in this blending ratio regime. In the case of ITIC there is a moderate up shifting as its fraction in the film decreases. Consequently, the analysis of the Raman shifts in PTB7-Th:ITIC:PC70BM blends indicates that the optimum composition corresponds to a morphology consisting of well-mixed donor:acceptor domains with about 15%–30% polymer content (large mode shifts), together with relatively pure (small mode shifts) domains of the two acceptors.

It is insightful to look at the same sample before and after annealing (Figure 4 and Figure S7, Supporting Information). A second optimum composition emerges within the phase diagram. In this case, annealing places the second optimum at higher fullerene contents, which could be a result of its more favorable steric interdiffusion through the film and subsequent improvement in the extraction of charges. An optimum composition dependent on the thermal treatment has also been observed for binary systems.

To show the generality of the high-throughput methodology, in the next series of experiments we extended the ternary blend library generation and colocal acquisition of Raman/PL/Absorption and photocurrent maps to two additional ternary blend systems, namely, PBDB-T:ITIC:PC70BM and P3HT:O-IDFBR:O-IDTBR (see Figure 6). In both cases, the devices were fabricated following the procedures described above, and changing the ordering of the acceptor layers to broaden the area covered in the ternary diagrams (see the Experimental Section). The extended data for these systems can be found in Figures S8–S12, Supporting Information.

Figure 6a shows that for PBDB-T:ITIC:PC70BM blends the highest performance corresponds to blending ratios spanning between 10 and 30 vol% of PC70BM loading. More specifically, the photocurrent maximum locates at a blending ratio of 0.45:0.30:0.25 (v:v:v, PBDB-T:ITIC:PC70BM). The here obtained optimum blending ratio is in very good agreement with what has been recently found in ternary spin coated devices, i.e., 0.5:0.4:0.1 (w:w:w, PBDB-T:ITIC:PC70BM).[23] (Note that converting from volume to weight percentage can easily be done when the material densities are known) In this system, the polymer has an almost overlapping absorption with ITIC, which in turn shows in the fact that both LBIC and WhiteBIC

![Figure 6](https://example.com/figure6.png)

Figure 6. Ternary composition diagrams of the regions with the highest performance corresponding to a) two PBDB-T:ITIC:PC70BM devices processed changing the coating order of the acceptor materials; and b) two RR-P3HT:O-IDFBR:O-IDTBR devices processed changing the coating order of the acceptor layers and two extra devices processed following the two-drop processing method. The color scale corresponds to the photocurrent extracted under white light illumination.
Figure 7. Ternary composition diagrams corresponding to seven different RR-P3HT:O-IDFBR:O-IDTBR devices (~150 000 data points per plot). The color scale corresponds to a) photocurrent at 488 nm excitation; and b) Raman peak shift of RR-P3HT.

have a similar spatial distribution (Figures S8 and S9, Supporting Information). Moreover, the contribution to the total photocurrent of relatively long wavelengths (633 nm) is larger than that of higher energies (488 nm), as seen in the corresponding LBIC maps and as expected by the corresponding absorption profiles. A series of samples with fixed stoichiometry has also been fabricated and are shown in Figure S12 (Supporting Information).

Regarding RR-P3HT:O-IDFBR:O-IDTBR blends (Figure 6b), a single white light photocurrent maximum is obtained for a ratio of 0.5:0.4:0.1 (w:w:w). This value lies relatively far from what has been previously reported for spin-coated devices, i.e., 0.5:0.15:0.35 (w:w:w).[17] P3HT has a very large Raman cross-section that can yield higher uncertainties on the composition determination compared to the other systems. The deviation from published results is, however, larger than the expected uncertainty on our composition. Therefore, we believe that the discrepancy may be related to the known factors affecting the efficiency in this system, such as molecular weight of the polymer, different attained morphologies between spin and blade coating and/or actual differences in the optimum composition depending on the specific drying kinetics associated to each processing method. Similar to the case of PTB7-Th based ternaries, which show an annealing dependence optimum composition, we believe that morphology is the most likely cause of the observed shift. Evidence supporting a strong dependence of efficiency in morphology can be extracted from the almost three times larger PL shifts (Figures S10 and S11, Supporting Information) observed in this ternary compared to the other two.

In order to gain further insights into the observed discrepancy, an additional series of RR-P3HT:O-IDFBR:O-IDTBR samples were prepared. In this case, the samples were prepared in conventional geometry (ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/ternary/LiF/Al). For this ternary, the 488 nm LBIC maps are spatially well correlated with the WhiteBIC maps (Figure S10, Supporting Information), thus both techniques should lead to the same optimum compositions. For these experiments, we chose to measure the photocurrent at 488 nm excitation as it can be measured simultaneously with the Raman image from which composition is deduced, and so is the fastest exploration possible. Figure 7 shows the results for a total of seven (non-annealed) RR-P3HT:O-IDFBR:O-IDTBR devices and ~150 000 data points per plot. The large and statistically meaningful dataset included in Figure 7a yields an area of high performing blending ratios in agreement with the previous batch under white light illumination (Figure 6b). From this we conclude, first that the experiments are quite reproducible, and second, that our finding of a different maximum is not related to the sequential deposition producing large vertical phase segregation.

The Raman peak shift analysis of the RR-P3HT vibrational signature (Figure 7b) shows that the highest photocurrent occurs for moderate blueshifts (~4–6 cm⁻¹) with respect to a pristine RR-P3HT film, while both large (~10 cm⁻¹) and small (~0–2 cm⁻¹) blueshifts are detrimental for the device performance. Since at 488 nm excitation both crystalline and amorphous RR-P3HT domains contribute to the Raman scattered intensity,[31,32] these results indicate that the film morphology in RR-P3HT:O-IDFBR:O-IDTBR ternary blends, and more specifically the degree of crystallinity attained at the polymer domains, is critical to achieve high performance devices. Neither largely amorphous (large blueshifts) nor strongly crystalline (small blueshifts) RR-P3HT domains are favorable for the photovoltaic device performance. Instead, a tradeoff between their purity (improved percolation) and the degree of intermixing with the acceptors (improved charge separation) is needed, as suggested by the moderate blueshifts observed in the high performing areas of the phase diagram. So, it is possible that for non-annealed blade-coated devices, the degree of crystallinity of the components is hindered at the O-IDTBR rich compositions. A systematic annealing study, which goes beyond the scope of the current manuscript, would possibly help to clarify further the apparent discrepancy between our data and published data for the P3HT based ternary.

One useful observation deduced when comparing the three material systems is the fact that the high efficiency region spans over a relatively large area of the ternary phase diagram. One way to quantify this is to determine how many crossing points between composition lines are included in the red area of each sample: between two and five. In fact, the whole ternary surfaces are relatively smooth. In other words, if one explores the ternary phase diagram with 10% steps in relative composition, there are good chances to find at least two
samples close to the absolute maximum. A rational, resource saving, approach for optimizing ternary blends would then commence by exploring the phase space in 20% steps, which would result in four samples of one binary, another four samples of the other binary, and six ternaries. The ternaries should, however, be equally spaced in the phase diagram rather than following the D:A 1:1 trajectory. This exploration would define the region of interest for a zoomed in second round with six extra devices. A total of 20 devices would then be sufficient for a first evaluation of the potential of a new ternary. While our approach, which would use around four samples to cover the whole phase space, is more accurate and statistically meaningful, the 20 devices approach has the advantage that can be implemented in most labs working on the field.

Finally, we would like to remark that, clearly, in this first manuscript we have not fully explored all the information hidden within the large amount of data points and colocal measurements. These large, self-consistent, varied and statistically meaningful datasets might be of use for data science studies, and therefore we have made it available at the CSIC repository for other researchers to use freely (http://hdl.handle.net/10261/194041).

6. Conclusion

We have introduced a solution-based methodology to produce large libraries of organic solar cells that effectively explore the ternary phase diagram. Each sample covers ~15%–25% of the composition space with typically close to 5000 different composition/thickness values. Colocal hyperspectral images of such samples, which produced millions of data points, enables the correlation of performance with composition as well as local morphology. In particular, we show that Raman shifts are a useful tool to address the degree of mixing and purity of domains. Importantly, this broad exploration of the phase diagram enables the determination of the composition (and number) of performance maxima, which we find to sometimes lie outside the conventionally targeted D:A 1:1 trajectory. Our results were in relatively good agreement with a large series of devices fabricated with fixed composition. This type of high-throughput evaluation is, therefore, a very useful and timely contribution that will help to identify absolute performance maxima in promising multicomponent solar cells. Interestingly, the large body of data produced can open the possibility to use data science techniques in the development of solar cells through the availability of coherent and statistically meaningful data sets.

7. Experimental Section

Materials: Regioregular poly(3-hexylthiophene-2,5-diyl) (RR-P3HT) with average molecular weight of 20–45 kDa was purchased from Sigma-Aldrich, Lot# MKCD8731. Poly[2,6-(4,8-bis(2-ethylhexyl) thiophen-2-yl)-benzothiadiazole-2,5-diyl] (PTB7-Th), batch M261; [6,6]-Phenyl-C71-butyric acid methyl ester (PC70BM); as well as the indium tin oxide (ITO) substrates were purchased from Ossila. PEDOT:PSS was purchased from Heraeus. The ZnO nanoparticles dispersion was obtained from Avantama.

Sample Preparation: All materials were dissolved in chlorobenzene (CB), in a concentration range of 10–15 mg mL$^{-1}$ for the acceptors, and 15–20 mg mL$^{-1}$ for the donor polymers. Two opposite corners of the ITO coated substrates were etched with diluted HCl and solid Zn, to electrically isolate them and obtain one top and one bottom electrode per side. Then the substrates and cut glasses for encapsulation were cleaned by consecutive sonication baths in acetone, soap, isopropanol (5 min each), and sodium hydroxide 10 vol% (10 min), rinsing with DI water after each step. The top transport layer, either PEDOT:PSS or ZnO depending on the device architecture, was deposited using an automatic blade coater Zehnarter ZAA 2300 with an aluminum applicator Zehnarter ZUA 2000, in air conditions and at a constant speed of 5 mm s$^{-1}$. The drop volume used was 100 µL for PEDOT:PSS and 50 µL for ZnO. The temperature was set to 60 and 40 °C for PEDOT:PSS and ZnO, respectively. All active layer materials were deposited using a second blade coater equipment (same brand and model) that included custom-made electronics to enable speed gradients, inside a nitrogen-filled and dry glove box, at 80 °C, while setting a blade gap of 200 µm. The drop volume used was 50 µL for the donor polymer in the first layer, and 40 µL for the acceptors. The speed was set to 30 mm s$^{-1}$ for constant speed film processing, while a linearly decelerating speed ramp was configured from 90 to 10 mm s$^{-1}$ for the processing of a thickness gradient in the first layer as well as in the standard composition fixed devices. The bottom transport layer and electrode, either LiF/Al or MoO$_3$/Ag, were thermally evaporated at a rate of 0.1 Å s$^{-1}$ for the transport layer and 1 Å s$^{-1}$ for the electrode. Samples were encapsulated using a cut glass slide and epoxy resin, then cured with an UV lamp for 5 min. The annealing process, when done, was performed in the nitrogen-filled and dry glove box by placing the samples in a hot plate at 120 °C for 10 min.

Optical Measurements: Variable-angle spectroscopic ellipsometry (VASE) data were acquired at a minimum of three angles of incidence using a Sopralab GES-5E rotating polarizer spectroscopic ellipsometer (SEMLAB) coupled to a charge-coupled device (CCD) detector. The ellipsometric data were modeled using WinElli piece of software and the standard critical point model.

All the optical characterization measurements performed in functional devices (Raman scattering, PL, reflection, LBIC, and WhiteBIC) were acquired using a WITec alpha 300 RA + confocal Raman setup, coupled to an Olympus objective with 10X magnification (NA 0.25). The built-in lamp of the setup was used for the white light measurements. Two lasers centered at 488 and 633 nm were employed for the Raman, LBIC, and PL measurements. The light was focused through the thick (1.1 mm), ITO-covered glass substrates and the laser power reduced accordingly to avoid photodegradation and bleaching of the active layer (3-5 mW at 488 nm excitation). Samples were placed in a motorized stage and connected to a variable gain low noise current amplifier DLPCA-200 manufactured by FEMTO Messtechnik GmbH.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

high-throughput screening, layer-by-layer deposition, organic solar cells, Raman imaging, ternaries

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