1. Introduction

Ever since the discovery of the conductivity of polymers\(^1\) and their consequent application on solar light harvesting devices,\(^2\) the scientific community has devoted a significant amount of effort to increase the performance of this technology. At early stages of the development of organic solar cells the governing principles affecting the photovoltaic performance were thoroughly investigated. Important milestones include the discovery of an effective charge transfer between donor and acceptor type compounds, the introduction of the bulk heterojunction (BHJ) concept to alleviate charge extraction,\(^3,4\) and key strategies to control microstructure and optimize optical absorption.\(^5\) The knowledge gained in those early steps paved the path towards the synthesis of novel materials that resulted in improved devices presenting higher efficiency and stability,\(^6,7\) from power conversion efficiencies (PCE) in the range between 1% and 3% for workhorse materials such as poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) or poly(3-hexylthiophene) (P3HT) combined with soluble fullerenes,\(^6,7\) up to current PCE values exceeding 10% for several systems.\(^9\)\textendash13\) There is no specific fundamental limitation to organic materials that indicates that much higher values are not possible, and the number of potential candidates is nearly infinite. Indeed, the organic nature of the photocative materials offers a myriad of possibilities to modify their chemical structure; for the case of conjugated polymers, there exists a vast assortment of combinations depending on the choice of moieties, the bridging atoms, the length and branching points of the alkyl side chains, and the molecular weight, to name but a few. Using search engines to inspect the literature, we estimate that in the last ten years \(\approx 5000\) organic conjugated materials have been tested in BHJ solar cells, albeit only a few tenths have been studied and optimized in depth. While applied quantum theory can help to select promising candidates,\(^14\)\textendash16\) the final performance often depends on a number of issues difficult to predict a priori, such as solubility, miscibility of compounds, tendency to crystallize, exact energy levels in the blend, etc. In practice, this means that for a given promising backbone, a family of systems need to be tested, including different side chains, molecular weights, donor/acceptor combinations, etc.\(^17\) Within this large and uncharted spectrum of materials and processes, combinatorial screening methodologies are highly on demand to speed up their exploration while helping the technology to approach the theoretical Shockley–Queisser limit of \(>20\%\) PCE.\(^18,19\)\)

From the engineering point of view, three main aspects must be addressed for the evaluation of a material system for BHJ solar cells, namely the active layer thickness, the donor–acceptor (D:A) blending ratio and the nanoscale morphology (typically controlled by deposition conditions, thermal annealing, and use of additives). Ideally, those three variables can be optimized separately and to some extent it is usually an acceptable approximation; however, the full potential of a novel active layer material requires for fine tuning of the preparation conditions that take into consideration the subtle interplay between them.\(^20\) For instance, the optimum thickness is often found close to the first interference maximum, which is governed by the refractive index of the active layer; this, on
the other hand, will be a function of the D:A ratio (fullerenes typically have higher refractive index than polymers) and the degree of crystallinity (higher crystallinity results in higher density of optical dipoles). Another example is the fact that the optimum D:A ratio will be correlated to the morphology through the phase diagram, so both need to be optimized simultaneously. This fact results in a yet unresolved evaluation conflict: on the one hand, hundreds of homogeneous samples are required for a full evaluation of the potential of a new compound, on the other, only a few tenths of milligrams are typically synthesized of each novel compound.

Most of the highest solar cell efficiencies reported in the literature are obtained with devices where the active layer is spin coated. Spin coating offers an easy option to obtain homogeneous layers over a relatively small area in a highly reproducible manner; however, the waste of material is large and changes in composition or thickness are made over several substrates. One possibility to accelerate the screening of materials with respect to the conventional method was proposed by Schubert and co-workers who used a robotic arm to inkjet print devices with combinatorial variations of parameters. On top of the typical limitations of inkjet printing (such as the required fine control on ink formulation to avoid inhomogeneities derived from the coffee-ring effect and Marangoni flows, or nozzle clogging) the authors found that the fast drying of the small amounts of solution in the multi-vial configuration prevented a generally successful film deposition.

An important observation that can point to new optimization avenues is the fact that the fabrication of each device takes several orders of magnitude longer than its photovoltaic evaluation. For a parallel fabrication process (say ten samples, each with several pixels), the manufacture of laboratory scale devices takes a few hours per device while taking a J-V curve typically only takes a few minutes. Therefore, moving from a fabrication intense to a measuring intense evaluation protocol would significantly accelerate the evaluation time per compound while minimizing the material waste. The use of gradients has been suggested for this purpose. In this case, a film exhibiting a gradient of the parameters of interest is locally scanned to deduce the optimal value for the given optimization parameter. A two pump slot-die implementation has successfully demonstrated the potential of this type of gradients for the evaluation of novel compounds. Slot-die coaters integrated into roll-to-roll systems have, however, important limitations, as they require large amounts of material and the complexity of the equipment makes it very exclusive.

Thickness gradients can be easily fabricated by blade coating and indeed have been employed as a demonstration for the potential of gradients in the optimization of organic photovoltaics (OPV) and organic light emitting diodes (OLEDs) at laboratory scale.

The local evaluation of performance is typically done by using techniques such as light beam induced current (LBIC), micro-electroluminescence or lock-in thermography. While these techniques are commonly employed for other types of studies, such as degradation studies, they can be equally suited for the inspection of samples intentionally fabricated with lateral inhomogeneities. It is worth noting that there have been attempts to directly monitor the characteristics of 2D composition gradients and some of them studied the combination of thickness and temperature effects, or thickness gradient screening using discrete devices.

In this work, we advance a simple fabrication platform based on blade coating that enables the fabrication of thickness, composition, and morphology gradients. We then demonstrate its usefulness by preparing solar cells of three different systems with a composition gradient that reveals the optimum D:A blending ratio in a single substrate with minimal materials usage (<10 mg per material) and easy processing feasible with the existing infrastructure in most research laboratories in this field. With the information therein extracted, a second solar cell is prepared with the optimum D:A ratio and processed to show orthogonally oriented thickness and annealing temperature gradients. With this method, it is then possible to extract the optimum blending ratio, film thickness, and annealing conditions employing just two devices. The complete and thorough characterization of devices with gradients is done by combining only two different measurements. On the one hand, photocurrent images provide a correlation between position and photovoltaic performance. On the other hand, we use Raman scattering to elucidate the thickness and composition distribution within the active layer in functional devices, according to a recent methodology developed in our group. The spatially resolved performance, composition, thickness and temperature are then correlated in order to identify the optimum preparation conditions for a specific D:A pair. In our experiments, we employed less than 10 mg of each material for their complete evaluation, a value which is within the standard amounts synthesized in the first batch of novel materials. In addition, the use of 2D gradients contemplates the interplay between the optimization variables investigated (e.g., the combination between thickness and phase segregation at certain drying conditions).

2. Results and Discussion

The evaluation process for a new material system consists of three main steps. First, the reference data for each material is taken from literature or measured. These data consist of the complex refractive index and the effective Raman cross-section, which are required to characterize the gradient. These data only need to be obtained once, and then they can be used in the analysis of the given material in combination with any other complementary material or even in multi-component systems. The second step is the fabrication of the devices with gradients varying the parameters of interest. The third step is the measurement of the local device performance (photocurrent) and the local structure (thickness and composition). The second and third steps might be repeated for different gradients or combinations of gradients (2D gradient geometries).

In the present study, we have selected three well-known systems, namely PCDTBT, PTB7-Th, and PfdBT4T-2OD combined with the electron acceptor PC70BM. Such compounds have been relatively well studied in the past and demonstrated to yield high power conversion efficiencies as well as a reasonable stability. Importantly, by using well-known polymers, we can evaluate the methodology described herein; comparing the results to previous art and thus confirm its applicability.
2.1. Refractive Index and Raman Cross-Section

The optimization process proposed in this work starts by the acquisition of the complex refractive index \((n + ik)\) and Raman cross-section \((\sigma)\) of the materials under investigation, which then enable the characterization of the local composition and thickness by Raman scattering. By including this step in the methodology, we avoid the need for a very complicated fabrication protocol in which the composition and thickness are controlled with great accuracy. Instead, we use very simple solution fabrication tools which result in less control of the exact position and shape of the gradient, but then locally determine this gradient with good spatial resolution. Interestingly, if one is only interested in evaluating whether a parameter is important or not, this quantification might not be necessary. Moreover, in principle \(n, k\), and \(\sigma\) only need to be determined once for each material, and then used in any combination with any other material (e.g., other acceptors or ternary systems).

The complex refractive index is the input parameter in the subsequent modeling of the Raman-scattering images in functional devices. The optical constants were extracted by means of variable-angle spectroscopic ellipsometry. The films of the pristine materials showed a thickness gradient laterally cladded between two adjacent regions of constant thickness (the thinnest and thickest values). The same samples were used for the extraction of the corresponding Raman cross-sections, and serve as a first check of the solubility of the compound and wetting and drying properties of the solution. While in principle ellipsometry could be used to determine composition and thickness, confocal Raman spectroscopy provides (up to) diffraction-limited spatial resolution together with a much better fingerprinting capability compared to the visible absorption measured in the former. In this very first experiment, additional information is obtained such as the solubility of the material or the layer thickness derived from the concentration of the solution casted, which is mainly affected by the viscosity when working at the typical range of operating conditions in blade coating. The conditions employed to obtain thickness gradients are described in detail in the following section.

The refractive indices of PTB7-Th and PffBT4T-2OD are shown in Figure 1a, while those of PCDTBT and PC70BM are included in Figure S1 in the Supporting Information. These values are in the same range as the typical ones obtained for conjugated polymers and fullerenes. The extinction coefficient provides information related to the band gap of the different materials, as well as the strength of absorption. The thickness values obtained with ellipsometry were compared to those obtained via profilometry, so to ensure the validity of our optical description.

The same sample is then scanned using a confocal Raman scattering setup in order to obtain the Raman intensity dependence as a function of film thickness for the vibrational band in PTB7-Th and the mode in PC70BM. The solid lines stand for the fitted transfer-matrix model using the corresponding Raman cross-section as fitting parameter. The dashed lines correspond to the standard deviation of the fit.
dependence on film thickness. We have recently demonstrated that this dependency can be modeled using the transfer matrix formalism\textsuperscript{[10]} with the complex refractive index for the wavelengths of interest as input parameters, and the effective thin film Raman cross-section ($\sigma$) as a fitting parameter. The Raman spectra took at 488 nm excitation for the four materials used in this work are shown in Figure 1b, while the thickness dependence of the Raman intensity for PTB7-Th and PC70BM is depicted in Figure 1c. We express the Raman cross-sections as ratios with respect to $\sigma_{\text{PC70BM}}$, which constitutes the workhorse example of electron transporting small molecule in high performing organic solar cells. Therefore, the cross-section ratios found at 488 nm excitation in air read 1.9 ± 0.3, 1.3 ± 0.4, and 7 ± 1 for the 1490 cm\textsuperscript{-1} mode in PTB7-Th, the 1437 cm\textsuperscript{-1} mode in PFBT4T-2OD and the 1447 cm\textsuperscript{-1} mode in PCDTBT, respectively. These ratios are much lower than 30, the maximum value after which the Raman approach is not sensitive enough to quantitatively deduce the composition ratio for the whole range of compositions.\textsuperscript{[10]} The use of Raman spectroscopy to characterize the photovoltaic films is also limited to thickness values below the saturation regime of the Raman intensity as well as to materials combinations which do not suffer from large variations in the degree of order and crystallinity during the blending process. In the former case the technique is mainly limited by the penetration depth of the excitation wavelength, whereas in the latter case the analysis of the scattered intensity in blends that include (semi)crystalline polymers usually results in difficulties to deduce the thickness of the thin film with enough accuracy.

2.2. Casting Methodology

We have chosen knife coating, aka blade coating, as the main technique to produce samples with parametric gradients. In this technique, a metal blade applicator is used to extend a certain volume of solution by means of the relative movement of the knife over the substrate located underneath at a given distance (gap). The movement of the blade leaves behind a wet film which, after the evaporation of the solvent, becomes a relatively homogeneous solid layer. Although blade coating is a mechanically simple deposition technique, the resulting films show a high degree of homogeneity when the experimental parameters involved are properly adjusted due to the self-metering character of the technique. These parameters include the blade velocity, the total volume of solution forming the reservoir, the gap between substrate and blade, the substrate temperature during deposition and the concentration of the solution. Following previous work,\textsuperscript{[29]} we have altered our doctor blade electronics in order to control speed and acceleration of the blade throughout the coating process. The speed of the blade is typically the main factor affecting film thickness for given solution concentration and viscosity (typically increasing concentration and viscosity leads to thicker films). We observed that employing concentrations around 30 mg mL\textsuperscript{-1} of the blend in chlorobenzene:ortho-dichlorobenzene (CB:oDCB) 1:1 volume ratio and a temperature of the substrate of 100 °C yields films of similar thickness for most of the D:A materials employed. This fact is very relevant since it implies that approximate thickness values can be predicted for new compounds without the need to severely optimize the process, minimizing the amount of blend material required for testing the deposition conditions. Typically, a thickness gradient is first performed in these conditions, using 60 µL of solution and a velocity ramp that goes from 100 to 10 mm s\textsuperscript{-1} within 6 cm of sample. Generally, faster speed yields thicker films, so as the blade moves decelerating, a thickness wedge is obtained. As a second order effect, the thickness also depends on the amount of solution available during the deposition itself. Below some critical liquid amount, the film becomes thinner as the blade moves since less liquid is available in front of the blade. We found that employing a decreasing speed ramp allows for steeper thickness gradients than increasing the speed as the two effects add up. When using positive speed ramps, the resulting thickness gradients are significantly less steep, a fact that could be used to effectively zoom in at specific thickness regions that are of our particular interest. Using the aforementioned conditions combined with a decreasing speed of the blade yields films that are 300 nm on the thickest part and 30 nm on the thinnest. It is worth mentioning that nonpolymeric solutions (such as small molecules) require higher concentrations to achieve such thicknesses since the viscosity is significantly lower. An example of thickness gradient for PTB7-Th is depicted in Figure S2 in the Supporting Information.

The temperature at which the substrate and blade are held during the blading process can be employed to control the drying process, which in turn can affect the morphology adopted by the D:A blend. For the solvents and viscosity ranges employed, the thickness is not significantly changed by substrate temperature as long as the film dries within a few seconds. This relatively fast drying is required to avoid liquid equilibration throughout the substrate upon passing the blade. Other factors such as the blade–substrate gap affect the final thickness in a much smaller scale thus are kept constant in our experiments being 150 µm gap a good starting point. The amount of solution is in our case mostly determined by the fact that our substrates are 7.5 cm long, the size of a typical microscope slide, and using more solution results in the unnecessary waste of material whereas using less can lead to the incomplete coverage of the area of interest. Notice that considering that each film requires 60 µL of solution with a typical solid content of 20 mg mL\textsuperscript{-1}, only 1.2 mg of material is needed per film, and a single film already contains most of the required information regarding thickness effects of a specific blend. Interestingly, this method can be used for other applications beyond OPV optimization, including the study of the geometrical confinement on phase transition temperatures,\textsuperscript{[32]} determination of exciton diffusion lengths,\textsuperscript{[13]} fabrication of position sensitive photodetectors,\textsuperscript{[34]} or as miniature spectrophotometers based on microcavity resonators with a wedged active layer.\textsuperscript{[35]}

We extend here this method beyond thickness gradients to also include the preparation of films with D:A composition gradients. A simple method to achieve this is by employing the aforementioned doctor blade technique and casting simultaneously two or more drops of the pristine materials. In this process, as the blade moves, the two solutions mix, and upon drying a composition gradient approximately perpendicular to the direction of movement of the blade is created. We have
made a systematic evaluation of blade speed and temperature to obtain the processing window that results in gradients (Figure S3, Supporting Information). Interestingly, we found that the casting conditions (substrate temperature and blade velocity) selected during the processing of the composition-graded layer determine different processing regimes that are visually depicted in Figure 2 as a phase diagram. For a given speed, increasing temperature accelerates the drying of the solutions. For slow drying, fully mixed films are produced. When drying is too fast, no mixing is observed. There is an intermediate region of drying in which a gradient is found. The exact conditions will clearly depend on the solution rheology, boiling point and its wettability on a given substrate. Despite being a relatively narrow range of conditions, we found them to be applicable for a large number of materials such as those presented in this manuscript and others currently under investigation like nonfullerene acceptors.

Figure 3 shows the Raman characterization of graded films for the aforementioned deposition conditions. Raman images were taken through the glass on complete devices. The Raman cross-sections deduced above were used to analyze the corresponding images in order to produce composition and thickness maps. All Raman data was took at 488 nm excitation in air and through the glass substrate.
Beyond the optimization of blends for OPVs, the presented properly mixed regions in the final film. More sophisticated final solid solutions. These two parameters are critical to obtain processing properties, including boiling point and rheology of the we present is suitable for combinations of materials that can either the pristine materials or 1:9 (w:w) and 9:1 (w:w) blends 1:1 (w:w) blend (mixed during hours) and the exterior drops are with a three drops extension, in which the central drop is a temperature dependent, so keeping the substrate above the glass large to allow molecular diffusion. (Note that diffusion is tem- and solvent evaporates up to the point when viscosity is too ponders in the movement of the blade, the use of Raman to characterize the exact composition map enables a one-to-one correlation between device performance and composition, as we will see in the following sections. There are also some vari- ations in film thickness which, since they can be quantified, can be used to simultaneously look at composition and thickness gradients, as we will show.

It is important to note that the colors in the optical pictures arise from both absorption and reflection due to the strong Ag reflectivity in the visible spectral range. The use of colorimetry for the identification or quantification of local composition can be misleading due to the strong interference patterns present in a metallized thin film unless rigorous optical modeling is applied. This further justifies the use of Raman and transfer matrix modeling to spatially fingerprint materials with the relevant degree of accuracy (=5%).

The confocal Raman images analysis does not discriminate phase separation smaller than the spot of the laser (typically tenths of microns when measuring through the glass with a 10× magnification objective), and therefore, it is difficult to assess the quality of the mixing at length scales relevant to charge generation. Indeed, D:A blend solutions are often left to stir for several hours prior to using them to ensure intimate mixing. In our case, mixing is done relatively quickly during deposition: the two drops of pristine materials mix within seconds as the blade bring them together during its movement and solvent evaporates up to the point when viscosity is too large to allow molecular diffusion. (Note that diffusion is tempera- ture dependent, so keeping the substrate above the glass transition of the polymer would enable further fullerene dif- fusion.) In order to evaluate possible differences coming from the very different solution mixing times, we have compared the photovoltaic performance of the described two drops method with a three drops extension, in which the central drop is a 1:1 (w:w) blend (mixed during hours) and the exterior drops are either the pristine materials or 1:9 (w:w) and 9:1 (w:w) blends if their viscosity does not allow for a good mixing within the time interval of the casting. Overall, the casting methodology we present is suitable for combinations of materials that can be dissolved and deposited using solvents with similar process- ing properties, including boiling point and rheology of the final solid solutions. These two parameters are critical to obtain properly mixed regions in the final film. More sophisticated mixing stages or casting conditions might be necessary for materials or solvents with strong tendency to phase-segregate. Beyond the optimization of blends for OPVs, the presented method could be used for any application in which the com- position needs to be investigated, such as white OLEDs based on ternary systems with cascading energy levels[36] or determination of phase behavior and phase diagrams in multicomponent systems.[37]

2.3. Donor:Acceptor Blending Ratio Optimization

A standard protocol for optimization of the different para- meters in OPV does not exist. In most research articles only the optimized parameters are given but the series of experi- ments leading to those optimum values is not often described. Here we choose to start by looking at the effect of composi- tion. This is motivated by the fact that the range of optimum D:A compositions for the different materials found in litera- ture spans between 1:4 to 2:1 in w:w ratios (i.e., from 80% to 33% in weight of the fullerene content). This range of poten- tial optimum values is very broad, the cells performance often sharply depends on the exact composition, and the optimum is difficult to predict beforehand as it depends on the interplay between the absorption of each component, degree of mixing, percolating pathways, and balance of charge carrier mobili- ties. The optimum thickness, on the other hand, often coincides with the first interference maximum (80–120 nm) for the absorbed electric field intensity. Moreover, the derivative close to the maximum is usually very smooth, meaning that using the conditions that yield 100 nm of active layer thickness it would likely be close to the optimum solution. Some materials with good transport properties and low level of unintentional doping would exhibit a PCE maximum close to the second interference maximum (≈250 nm), so it is clearly important to look at thickness, but not to start with. The optimum thermal annealing would also be strongly linked to the exact composi- tion through the phase diagram of the blend, and thus it makes sense to either look at it after optimizing the composition, or simultaneously within a 2D gradient.

In order to find the optimum blending ratio, a solar cell was prepared with a composition gradient ranging from pure donor to pure acceptor that includes all possible ratios in a single sub- strate, following the experimental protocol explained above. Optical and Raman images of the resulting layers with a com- position gradient are depicted in Figure 3 for PCDTBT:PC70BM and PTB7-Th:PC70BM blends. As already mentioned, in both cases there is a composition gradient along the short axis in which the top side contains 100% polymer and the bottom 100% PC70BM. The resulting devices are characterized by means of LBIC to obtain a local photocurrent map[38–40][Figure 4]. The photocurrent images show that there is a central band that extends along the long axis of the substrate which corresponds to the area with the highest photocurrent generation. This result is in agreement with the Raman data that suggest that D:A mixing does occur during the casting of the active layer and that a composition gradient is obtained as indicated by the low photocurrent observed close to the substrate edges, where the composition is close to the pure cases. Since the LBIC maps illustrated in Figure 4 are corrected for excitation light intensity fluctuations, the differences in photocurrent can be ascribed to changes in composition, modulated by the small variations in
film thickness. In order to separate the effect of both variables on the photocurrent, we use the quantitative Raman maps that were described in the previous section which were collected exactly on the same devices. The local photocurrent mapping from LBIC can then be spatially correlated with the thickness and composition data extracted from the Raman-based images. For visualization purposes, the results are plotted eliminating the spatial dependence, which allows for a rapid spotting of the optimum thickness and blending ratio conditions of the active layer (Figure 5).

As it can be observed in Figure 5, for the PCDTBT:PC70BM blend there exists an optimum active layer thickness around 90 ± 10 nm and an optimum polymer volume fraction of around 20 ± 10 vol% which yield the highest photocurrent. The obtained polymer volume fraction corresponds to a D:A ratio of ≈1:4 (w:w) according to the reported density of the materials. Similarly, for the PTB7-Th:PC70BM blend (Figure 3b) there is an apparent optimum thickness of 100 ± 10 nm and a polymer volume fraction of around 50 ± 10 vol%, which corresponds to a D:A ratio of 1:1.5 (w:w) (considering \(\rho_{\text{PC70BM}} = 1.72 \text{ g cm}^{-3}\), \(\rho_{\text{PTB7-Th}} = 1.17 \text{ g cm}^{-3}\) and \(\rho_{\text{PCDTBT}} = 1.15 \text{ g cm}^{-3}\)). The D:A ratio can be obtained assuming that the density of both materials is homogeneous and invariant upon the blending process. Both D:A ratios found with this methodology agree very well with the reported values in the literature, thus giving validity to the methodology.

The uncertainty in volumetric optimum composition, partially arising from slightly different thicknesses, is of the same order than that of the accuracy of the Raman quantitative analysis. Typical density values for conjugated polymers are around 1.1 to 1.3 g cm\(^{-3}\). This relatively narrow range (±10%) of density values could be used to safely infer a reasonable density value for a new compound of yet unknown density in order to convert between volume and weight fractions.

In order to evaluate the generality of our developed technique, we have fabricated PffBT4T-2OD:PC70BM blend films with a composition gradient. The corresponding devices were measured with Raman and LBIC (Figure S4, Supporting Information). The volumetric composition was similarly extracted by means of Raman spectroscopy using the Raman cross-sections of the materials as discussed above. An optimum D:A volume ratio of 1:1 was obtained, which corresponds to a weight ratio of 1:1.5 (w/w) considering \(d_{\text{PffBT4T-2OD}} = 1.17 \text{ g cm}^{-3}\). This optimum composition value is in agreement with the values reported for the best performing devices fabricated with the PffBT4T-2OD:PC70BM blend. The quantitative analysis of the Raman-scattered light yields, however, inconsistent thickness values. The reason for this mismatch in the quantification of the thickness is currently under investigation but it is possibly related to variations in the refractive index upon blending, as well as the intrinsic limitations of the Raman quantification analysis detailed in the literature.

The composition gradient films implicitly include the effect of the active layer thickness on the extracted photocurrent for a
limited range of thickness values. A full exploration of this parameter can be performed by casting a film of constant D:A ratio, ideally using the values found in the previous experiment. This second sample allows to evaluate the photocurrent at the first two interference maxima, as well as to provide full PCE values, as we will show. Therefore, once the optimum ratio between the donor and the acceptor materials is found, such variable is kept constant while the thickness and the annealing temperature are optimized in separate substrates with their corresponding gradients.

2.4. Thickness Gradient Optimization

In order to confirm the results found in the previous experiments and validate the methodology, discrete solar cells were prepared over a thickness wedged active layer device. The specifics for the preparation of a varying thickness active layer are explained in detail in the experimental section. Discrete solar cells allow for the characterization of parameters such as open circuit voltage ($V_{oc}$), current density ($J_{sc}$), fill factor (FF), and PCE. Along the thickness gradient, a large area electrode was also deposited on the same substrate (Figure S2d, Supporting Information). This allows measuring LBIC over the whole thickness gradient with a much higher lateral resolution, in this case 100 μm as dictated by the dimensions of the laser spot. For comparison purposes, the thickness for this sample was obtained by mechanical profilometry at equidistant points along the active layer. This simple experiment reveals the profile of the active layer thickness. The combination of LBIC data over the long metallic electrode (Figure 6a) and $JV$ curve scanning of discrete devices within the same substrate (Figure 6b) provides useful information about the relationship between efficiency and (LBIC) measured photocurrent.

Figure 6b summarizes the PCE and $J_{sc}$ results extracted from the $JV$ curves of the 12 different 8 × 2 mm² individual solar cells under 1 sun 1.5 AM-G calibrated illumination. It is important to remark that for this experiment, the indium tin oxide (ITO)-covered substrate has a specific pattern to isolate the contacts of each individual device. The thickness gradient of the active layer covered a distance of 6 cm and spanned from ≈40 to 250 nm for both materials.

For the PTB7-Th:PC70BM binary, thickness has a relatively large effect on efficiency. The optimum thickness is found within a relatively small range, between 100 and 130 nm. Furthermore, the $J_{sc}$ oscillates with thickness showing an absolute maximum at ≈150 nm and a second relative maximum at ≈270 nm. On the other hand, the PCDTBT:PC70BM binary shows a smooth increase in photocurrent and efficiency until ≈100 nm and then reaches a plateau up to ≈250 nm. For the D:A material systems explored in this work the values found for the optimum thickness are in agreement with previous results reported in the literature, as well as the results obtained from the composition gradient devices discussed above.[49] The procedure employed for the preparation of the reported inverted solar cells yields efficiencies in line with the values found in the literature for these D:A pairs when the optimum conditions are met.

Figure 6 indicates that in the case of the PCDTBT:PC70BM blend the photocurrent (which is directly proportional to the external quantum efficiency (EQE) in Figure 6a) measured in the continuous part of the device matches very well the discrete device performance in terms of PCE (solid green curve in Figure 6b) all over the thickness regime explored (from 50 to 250 nm). Such thickness regime covers two interference maxima in the photocurrent albeit only that occurring at ≈100 nm yields the highest PCE in the discrete devices of ≈5%. Due to limitations in charge transport, thicker films may have reduced fill factors, which means that even when the photocurrent might be high, the overall PCE may not. Although the open circuit potential is not significantly affected by film thicknesses ranging from 30 nm to several hundreds of nanometers, there exist cases in which the open circuit voltage depends on composition, such as in the recently published ternary alloys.[50,51] The proposed methodology of this manuscript which is based...
on first, preparing a gradient of composition and thickness with a common electrode, and then a thickness gradient with an array of discrete pixels presents a solution for any $V_{oc}$ discrepancies affecting the final result. Alternatively, it has been demonstrated the possibility of using a mobile top electrode, such as that proposed by Savagatrup and co-workers.[67]

One aspect that is also evident from our thickness graded samples is the fact that a Fabry–Pérot interference of the incident light between the glass and the metallic electrode occurs and has the potential to enhance light absorption within the active layer when the right conditions of layer thicknesses are achieved. Many studies have been developed to predict the exact thickness that could result in some light trapping that would enhance the incident photon-to-current efficiency; however, achieving such thicknesses typically follows a trial and error approach with spin-coating that is highly resources intensive. In our case, the natural smoothness of the gradient thickness yields all the possibilities in a single, self-referencing sample, thus allowing validating the theoretical models, and vice versa. In fact, the high control of the layer gradient slope has made possible the fabrication of organic near-IR microcavity based spectrophotometers where the spectral response is strongly determined by the active layer thickness.[35]

For the PCDTBT:PC70BM thickness gradient sample an optical picture of the reflection already shows relatively strong interference patterns from white light as it can be seen in Figure 6a. When the optical image is compared to the corrected photocurrent measured along the thickness wedge, some correlation can be perceived. Apparently, the regions where the reflection is orange on the picture inset also present higher photocurrent, which could be indicative of an enhanced light trapping. This kind of interference effects are taken into account in the modeling of the Raman-scattered light in functional devices. The thickness dependent data for four different material combinations is shown in Figure S2 in the Supporting Information.

2.5. Morphology Optimization

We further tested the effect of annealing temperature over a homogenous thickness and composition active layer device. The temperature gradient was achieved with a calibrated Kofer bench that provides a controlled temperature gradient of approximately 1 °C mm$^{-1}$. In this experiment, the annealing process was performed prior to the metallic electrode deposition to avoid the disruption of the temperature gradient that a highly thermally conductive electrode might produce. Although ITO could have a similar effect, its thermal conductivity is lower than silver (5 vs 406 W m$^{-1}$ K$^{-1}$, respectively)[52,53] and allows keeping a controlled temperature gradient.

Figure 7 illustrates the photocurrent of 2 mm wide solar cells separated by 2 mm disposed along the temperature gradient for two PCDTBT:PC70BM devices where the active layer was cast at different temperatures and then placed on the Kofer bench for 10 min. According to Figure 7 there is not a significant dependence on the casting temperature (at least within the temperature range explored), which is indicative that morphology of the film does not strongly depend on substrate temperature for this system; however, annealing beyond 75 °C results in a decrease of the photocurrent by about half compared to a mild annealing of 10 min at 70 °C where the photocurrent observed shows a maximum. This annealing study is in agreement with the results found in previous works.[54]

An alternative method to control the nanoscale morphology is the use of solvent additives. Our methodology could be used to explore if an additive has an effect on the performance of the solar cells. We have, for instance, fabricated a PTB7-Th:PC70BM sample containing a gradient of additive by depositing three drops with 0 vol%, 5 vol% and 10 vol% of 1,8-diodooctane (DIO). The resulting LBIC is shown in Figure S5 in the Supporting Information, which clearly demonstrates a strong influence of the performance with DIO content, being the optimum in the range between 0 vol% and 5 vol%. An exact quantification cannot be made using Raman, as the additive leaves the sample and there is not a significant Raman band shift derived from variations in the film morphology. A very crude linear approximation of the additive content within the sample suggest a concentration of about 3%, which reassuringly is very close to the reported optimum. Further work needs to be carried out to find a measuring tool that allows quantifying the local amount of additive during the deposition itself.

2.6. Single Substrate Double Gradient

The here presented technique offers the possibility to generate orthogonal gradients spanned over the two axes of the substrate. In this particular case we prepared a sample showing a thickness gradient in its short axis and an orthogonally oriented thermal annealing gradient in its long axis. This approach has the added benefit of the simultaneous testing of both variables,
a type of evaluation that is very resource intense when using conventional evaluation protocols via multiple substrates with homogeneous active layers. In addition, it aids in the comparison of the effect in the performance of both variables since external fluctuations are intrinsically kept constant, e.g., differences in the interlayers or in the active layer solution occurring from batch to batch.

For this experiment, a sample was prepared by blade coating a thickness gradient along the short side of the 7.5 × 2.5 cm² substrate. The solution casted was the same employed for the previous thickness and thermal annealing isolated experiments. Before the deposition of the back contact a gradient of annealing temperature along the long side of the substrate was performed by means of a Kofler bench placed inside a glove box. Subsequently, LBIC and Raman imaging were employed to map the surface properties with a lateral resolution of 100 µm.

Figure 8a–c shows the LBIC photocurrent maps for PCDTBT and PTB7-Th based devices, respectively. It can be appreciated that the active layer thickness has a larger impact on the photocurrent than annealing for these two systems. In fact, post deposition annealing does not have any appreciable effect on P3HT:PCBM blend based solar cells (Figure S4, Supporting Information), while thickness clearly has a strong influence on performance. Coming back to PCDTBT-based cells, we note that there is a nonlinear response of the films to the annealing temperature, since there is a small increase in the photocurrent at intermediate temperatures. This is in accordance to the results of discrete cells shown in Figure 7, where a small increase of performance was observed at 110 °C. This demonstrates that using temperature gradients results in high sensitivity to small temperature intervals at which there might be strong effects in performance.

The results here obtained are in agreement with the information extracted from the single gradient devices investigated above. Therefore devices based on 2D gradients open the door to further savings in time and resources.

2.7. Time and Resources Saving Analysis

The main motivation of this work deals with the development of a technique that can noticeably reduce the time and resources required to optimize novel OPV materials, thus accelerating the progress of this technology. On one hand, based on available literature, we estimate that the conventional sample-by-sample method requires at least 6 substrates with different D:A ratios to determine approximately the optimum composition window; at least 12 substrates to estimate the optimum active layer thickness; and at least 6 substrates with different annealing temperatures. On the other hand, by following the here presented combinatorial methodology we have demonstrated that the optimization can be performed using a single substrate for each variable (in the best scenario). Therefore, we estimate that using gradients instead of discrete samples reduces the usage of material by at least a factor of 5.

In terms of timesaving (S), the quantification can be performed according to the following ratio

\[ S = \frac{N_{\text{dev}} (t_{\text{fab}} + t_{\text{Jv}})}{t_{\text{fab}} + N_{\text{dev}} t_{\text{LIC}}} \]  

where \( N_{\text{dev}} \) is the number of discrete samples fabricated (24 for the example above), \( t_{\text{fab}} \) is the average time required to fabricate each device (1.7 h per device in the best case if the fabrication is performed in batches of nine devices in parallel; see the
Supporting Information for details on the estimation of the fabrication time based on the authors' experience working on four different international labs, $t_{JV}$ is the time required to measure the $J-V$ curve in a single homogeneous device (around 5 min), $N_{pts}$ is the number of photocurrent data points extracted at the LBIC setup and $t_{LBIC}$ is the time spent by the LBIC setup to measure a single data point. If we would like to obtain the same amount of information from the gradients that we normally do with the homogeneous samples, then $N_{dev} = N_{pts}$ and $S \approx N_{dev} = 27$. When acquiring photocurrent maps in lateral steps of 200 µm, $N_{pts} \times t_{LBIC}$ equals ≈2 h, thus with these typical values $S$ equals ≈13. This result indicates that the use of gradients instead of discrete devices as the optimization procedure in OPV devices leads to more than a 10-fold reduction in the required experimental time for evaluation.

In addition to the time and resources efficiency, the amount of information that can be obtained from gradients is much higher (denser) than the one obtained from discrete samples. On the one hand, the availability of a much larger amount of data helps to perform meaningful statistics on the relevant parameters minimizing the sample to sample variability. On the other hand, our methodology can probe combinations of parameters that would be unfeasible to consider if using a conventional sample-by-sample methodology. As an example, LBIC maps provide information coming from hundreds of active layer thickness, composition and/or annealing combinations whereas a discrete sample exclusively provides averaged information from a single combination of such parameters. For a deep optimization protocol in which 2D combinatorial arrays are made of homogeneous samples with gradual changes in the relevant parameters, $N_{dev}$ quickly would reach ≈100, and in that case, our methodology would be almost 50 times faster than the conventional method.

3. Conclusions

In this work we have introduced a combinatorial screening methodology to optimize the performance in bulk heterojunction organic solar cells. The procedure minimizes the usage of resources and experimental time while leading to the same optimum parameters obtained following the traditional sample-by-sample methodology. Each donor:acceptor (D:A) pair explored in this work required a minimum of two graded devices (a composition gradient and an active layer thickness/annealing double gradient) to be fully optimized. The optimum values are found using a combination of a quantitative model to confocal Raman spectroscopy images with photocurrent maps. The spatial matching of both datasets serves to quickly spot the optimum window of the relevant parameters (blending ratio, active layer thickness and annealing temperature) that yield the optimum device performance. The final PCE values obtained were 5%, 8%, and 9.5% for PCDTBT:PC70BM, PTB7-Th:PC70BM, and PffBT4T-2OD:PC70BM, respectively.

We have estimated that the here presented combinatorial methodology implies a 5-fold and an ≈10–50-fold reduction in the usage of resources and time, respectively, compared with sample-by-sample methodologies, thus facilitating the fast and efficient evaluation of novel materials that are synthesized in minimal amounts (<10 mg). This combinatorial approach will certainly accelerate the identification of highly efficient D:A pairs and contribute to the ongoing progress of the OPV technology. Interestingly, the methodology can be easily extrapolated to the optimization of other device layers or processing parameters, such as the thickness of the electron and hole transport layers as well as the content in processing additives required to maximize the device performance.

4. Experimental Section

Materials: Poly[N-(3′,6′-heptacarbazole-alt-5,5′-4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]] (PCDTBT) was obtained from Ossila, batch 1311, CB fraction. Poly[4,8-bis(S-(2-ethylhexyl)thiophen-2-yl)]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl))-3-fluorothieno[3,4-b]thiophene-2-carboxylate-2,6-diyl)] (PTB7-Th) was obtained from Ossila. Poly[(5,6-difluoro-2,1,3-benzothiadiazole-4,7-diyl)-alt-(3,3′-di(2-octyldodecyl)-2,2′,5,5′-terthiophen-4,7-diyl)] (PFBT4T-2OD) was obtained from Ossila, batch M301. [6,6]-phenyl C71 butyric acid methyl ester (PC70BM) was obtained from Solenne BV. ZnO nanoparticles were synthesized following the procedure published elsewhere.[55] Patterned ITO substrates, cover slides and UV-curable epoxy were purchased from Ossila. All materials were used as received.

Sample Preparation: For the temperature and thickness gradient solar cells, PCDTBT was dissolved in CB at a concentration of 15 mg mL$^{-1}$ and mixed with PC70BM at a concentration of 10 mg mL$^{-1}$ for a total solid content of 20 mg mL$^{-1}$. For PTB7-Th, it was dissolved in CB mixed with PC70BM at a weight ratio 1:1.5 for a total solid content of 35 mg mL$^{-1}$. For PFBT4T-2OD, it was dissolved in CB:ODCB 1:1 mixed with PC70BM at a weight ratio 1:1.2 for a total solid content of 20 mg mL$^{-1}$, the solution was stirred overnight at 80 °C. ITO coated substrates with patterned electrodes and cut glass microscope slides were cleaned by consecutive sonication for 15 min in acetone, water with detergent and isopropanol, rinsing them with water after the detergent step. Following the solvent cleaning they were treated with ozone for 20 min. For the PCDTBT composition gradient separate solutions containing 20 mg mL$^{-1}$ of polymer and PC70BM were prepared in CB, then casted at a speed of 10 mm s$^{-1}$ with the substrate at 100 °C and using 50 µL of active layer solution. For the PTB7-Th and PFBT4T-2OD composition gradient, separate solutions containing 15 mg mL$^{-1}$ of the polymer and 25 mg mL$^{-1}$ of PC70BM were prepared in CB:ODCB 1:1 and then casted at a speed of 7 mm s$^{-1}$ with the substrate at 100 °C using 60 µL of active layer solution. Knife coater equipment consisted of an automatic coater Zehntner ZAA 2300 and an aluminum blade Zehntner ZUA 2000.

Light Beam Induced Current: LBIC was measured on a custom-made system. The sample was located on a motorized X, Y, and Z stage, and illuminated locally by a 532 nm laser (Thorlabs, CP5352). After passing through a multimode optical fiber and a beamsplitter (Thorlabs, EBS1), the laser was focused on the device using a long working distance 20x Mitutoyo objective. The incident light intensity was monitored with a photodiode power sensor (Thorlabs, S120VC) connected to a digital power meter (Thorlabs, PM100D). The short circuit current was monitored with a multimeter (Keithley 2400 SourceMeter). Data was acquired using custom software that allowed keeping the sample plane in focus and the diameter of the laser spot below 30 µm.

Raman imaging: Raman scattering images were acquired using a WITec alpha 300 RA+ confocal Raman setup. The samples were placed on a combined step motor/piezo stage and excited through a 10× objective using a solid state laser centered at 488 nm. Images were analyzed using WITec Project FOUR software. The quantitative modeling of the Raman-scattered light was performed using home-made fitting routines in MATLAB.

Ellipsometry: Variable angle spectroscopic ellipsometry was performed using a VASELAB GESS rotating polarizer ellipsometry. At least three angles of incidence were collected for each sample, and two different film thicknesses were analyzed. Fitting of the experimental data was
performed using the Standard Critical Point model implemented in the Winellii piece of software.

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.

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