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Effect of Solvent Additives on the Morphology and Device Performance of Printed Nonfullerene Acceptor Based Organic Solar Cells

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Supporting Information

ABSTRACT: Printing of active layers of high-efficiency organic solar cells and morphology control by processing with varying solvent additive concentrations are important to realize realworld use of bulk-heterojunction photovoltaics as it enables both up-scaling and optimization of the device performance. In this work, active layers of the conjugated polymer with benzodithiophene units PBDB-T-SF and the nonfullerene small molecule acceptor IT-4F are printed using meniscus guided slot-die coating. 1,8-Diiodooctane (DIO) is added to optimize the power conversion efficiency (PCE). The effect on the inner nanostructure and surface morphology of the material is studied for different solvent additive concentrations with grazing incidence small-angle X-ray scattering (GISAXS), grazing



incidence wide-angle X-ray scattering (GIWAXS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Optical properties are studied with photoluminescence (PL), UV/vis absorption spectroscopy, and external quantum efficiency (EQE) measurements and correlated to the corresponding PCEs. The addition of 0.25 vol % DIO enhances the average PCE from 3.5 to 7.9%, whereas at higher concentrations the positive effect is less pronounced. A solar cell performance of 8.95% is obtained for the best printed device processed with an optimum solvent additive concentration. Thus, with the largescale preparation method printing similarly well working solar cells can be realized as with the spin-coating method.

KEYWORDS: printed organic solar cells, high-efficiency organic solar cells, solvent additives, slot-die coating, small molecule acceptor

1. INTRODUCTION

Organic solar cells have gained significant interest as a renewable energy source in industry and research during the last years.¹⁻⁷ Compared to conventional silicon based photovoltaic devices, organic solar cells can be lightweight, flexible and transparent which enables to cover a broad field of potential applications in architecture and daily life, e.g., organic solar cell windows, roofs, trees, and even clothing.^{8–11} Toward commercialization, an optimization of the solar cell performance and development of a large-scale production are necessary.¹²⁻¹⁸ Current research focuses on identifying new high-efficiency polymers in combination with suitable acceptor molecules.^{19–30} To date, spin-coated small-area organic solar cells reach record power conversion efficiency (PCE) values above 16%, which is already above the threshold for commercialization.³¹⁻³³ At present, the main challenge is the scale-up of the thin layer deposition in order to enable a lowcost production of large-area photovoltaic panels.^{34–36} Printing of active layers with a meniscus guided slot-die coater will be a possible way to overcome this challenge within the next years, because this method is compatible with roll-to-roll production.^{14,37} Unfortunately, the fundamentals of spin-coating and printing differ significantly and the film formation during spincoating differs from that during printing. As a consequence, the knowledge gained from one thin layer deposition method such as spin-coating cannot simply be transferred to the other method such as printing.^{34,38,39} A fundamental understanding of the processes during printing is needed and an optimization of printed organic solar cells by morphology control is indispensable.

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Figure 1. (a) Horizontal line cuts of 2D GISAXS data (black dots) and modeling results (red lines) obtained for printed active layers with different DIO concentrations in chlorobenzene solutions (0.00, 0.25, 0.5, and 1.0 vol % DIO from bottom to top); (b) average domain sizes for different DIO concentrations obtained from modeling; (c) average distances in the BHJ structure for different DIO concentrations. Splines (b and c) are guides to the eye.

In this work, the conjugated high-efficiency polymer poly[(2,6-(4,8-bis(5-(2-ethylhexylthio))-4-fluorothiophen-2yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)], denoted PBDB-T-SF, and the nonfullerene small molecule acceptor 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno-[1,2-b:5,6-b']dithiophene, denoted IT-4F, are printed out of chlorobenzene at room temperature with a meniscus guided slot-die coater⁴⁰ (Figures S1 and S2). The conjugated polymer PBDB-T-SF and the nonfullerene small molecule acceptor IT-4F are chosen as suitable materials to print high-efficiency organic solar cells due to their molecular structures being designed to feature ideal solar cell properties as seen before in spin-coated devices.¹⁹ Compared to the precursor species (PBDB-T and ITIC), the introduction of fluorine further improved the power conversion efficiency from 11% to 13% in case of spin-coated devices.^{19,41,42} The downshift of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) resulting from the fluorination, facilitated the charge transport and reduced the Coulomb potential between holes and electrons.¹⁹ Therefore, exciton splitting and charge transport are facilitated whereas exciton recombination is reduced. 1,8-Diiodooctane (DIO), a solvent additive widely used to improve the device perform-ance of spin-coated organic solar cells, ^{1,43,44} is added to the solution in order to enhance the PCE of the printed PBDB-T-SF:IT-4F devices. The influence of different DIO concentrations is studied and optimized conditions are identified. From a combination of scattering methods based structure determination and optoelectronic characterization a fundamental understanding of the impact of DIO is gained.

2. RESULTS AND DISCUSSION

The effect of DIO on the morphology of printed active layers for PBDB-T-SF:IT-4F solar cells is studied with grazing incidence small-angle X-ray scattering (GISAXS), grazing incidence wide-angle X-ray scattering (GIWAXS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The influence of the structure on the optical properties is analyzed with photoluminescence (PL), UV/vis spectroscopy and external quantum efficiency (EQE) and the correlation with the PCE is studied in the following.

2.1. Morphology of Printed Active Layers. The donor polymer PBDB-T-SF is mixed with the small molecule acceptor IT-4F in a 1:1 ratio and printed out of chlorobenzene with different concentrations of DIO using a meniscus guided slot-die coater (Figure S1). The dry thin films have a thickness of around 100 nm which is ideal for organic solar cells.¹⁹ GISAXS and GIWAXS measurements are performed to analyze the inner nanostructure of the bulk-heterojunction (BHJ) organic solar cells.⁴⁵ An incidence angle of 0.35° is chosen which is above the critical angle of the polymer and the acceptor molecule. This allows to probe the full film thickness and to gain insight into the inner structure. The application of grazing incidence geometry enables to measure thin films (e.g. 100 nm thickness) and enables to probe a larger sample area, thereby achieving a high statistical significance and quality.⁴⁶ In order to analyze the 2D GISAXS data (Figure S2), horizontal line cuts (Figure 1a) are performed at the critical angle (Yoneda region) of PBDB-T-SF.

Average domain sizes and distances in the bulk-heterojunction structure are obtained from modeling the GISAXS data with a model based on the effective interface approximation (EIA) of the distorted wave Born approximation (DWBA).^{47,48} According to the local monodisperse approximation (LMA), the overall scattering intensity can be described by the incoherent superposition of scattering intensities of individual domains in the thin film. The GISAXS data of printed active layers of PBDB-T-SF:IT-4F with different DIO concentrations are modeled with three substructures of cylindrical shape, which is a well-established approach to describe the polymer thin film morphology over a large range of length scales.^{3,49} Structure sizes (Figure 1b) and distances between domains (Figure 1c) in the BHJ structure are obtained by modeling the scattering data.⁵⁰ Results show decreasing average structure sizes and growing average



Figure 2. SEM (a-d) and AFM (e-h) images show the surface morphology of active layers printed with different DIO concentrations in chlorobenzene solutions: (a, e) 0.00, (b, f) 0.25, (c, g) 0.50, and (d, h) 1.0 vol % DIO.



Figure 3. GIWAXS data (dots) and modeling with Gaussian functions show an increase of the crystallinity due to the addition of DIO: (a) azimuthal q integral with marked (100) PBDB-T-SF and IT-4F, (010) PBDB-T-SF Bragg peaks and higher order Bragg peaks. The solid line is a guide to the eye. Tube cuts (dots) of the (b) (100) PBDB-T-SF Bragg peak and the (c) (100) IT-4F Bragg peak analyzed by fitting of Gaussian functions (solid lines). The gray bar masks the nonaccessible q-range.

distances with increasing DIO concentration. Active layers printed without solvent additive yield average structure sizes of (103 ± 1) nm, (39 ± 1) nm, and (11 ± 1) nm, whereas the addition of only 0.25 vol % DIO decreases the average structure sizes to (83 ± 1) nm, (29 ± 1) nm, and (10 ± 1) nm. This effect is favorable for the solar cell performance as the charge transfer from the polymer to the small acceptor molecule is facilitated by gaining interface area.⁴⁴ At higher solvent additive concentrations, the morphology is further altered. The average domain sizes are reduced to (79 ± 1) nm, (19 ± 1) nm and (9 ± 1) nm for 1.0 vol % DIO. This reduction of the average domain sizes can cause a decrease in the PCE due to a charge trapping assisted recombination mechanism.⁵¹

The average distances between domains grow from (200 ± 10) nm, (90 ± 10) nm, and (52 ± 8) nm in the case of

solvent-additive free active layers to (215 ± 10) nm, (130 ± 10) nm, and (53 ± 8) nm for thin films processed with 0.25 vol % DIO. An enlargement of distances between donor and acceptor domains can provoke charge stabilization and lower the probability of recombination by a reduction of Coulomb forces.^{15,52,53} Higher DIO concentrations of 0.50 vol % and 1.0 vol % result in the formation of average distances of (290 ± 10) nm, (138 ± 10) nm, and (54 ± 10) nm and respectively (300 ± 10) nm, (140 ± 10) nm, and (55 ± 8) nm. The significant increase of average domain distances with rising solvent additive concentrations obtained from the scattering experiment is supported by SEM and AFM.

SEM and AFM measurements of printed thin films of PBDB-T-SF:IT-4F are performed to image the structure at the sample surface for different DIO concentrations (Figure 2).

All films show a homogeneous film formation over the probed sample area. Active layers printed without solvent

additive show a network of cylindrical structures which are closely packed and even overlap (Figure 2a, e). The formation of large domains downsizes the interface area between donor and acceptor phase which is unfavorable for organic solar cells due to reduced charge transfer. For samples printed with DIO, smaller average structure sizes are formed which tend to form larger agglomerates and the domains occur less densely packed. In the AFM images, an increase of surface roughness is observed (Figure 2f-h). At a DIO concentration of 0.25 vol %, an interpenetrated network is formed, which facilitates the charge transfer from the electron donor polymer to the nonfullerene small molecule acceptor (Figure 2b,f). The slightly enhanced distances can provoke charge stabilization and minimize the undesirable effect of charge recombination at the interface.^{15,52} In active layers printed with DIO concentrations of 0.50 vol % (Figure 2c,g) or 1.0 vol % (Figure 2d,h), small structures are formed which agglomerate strongly provoking an increase in distances between domains and can elevate the risk of charge trapping in islands hindering charge transport to the electrodes.⁵

GIWAXS measurements are performed to analyze the crystalline part of the thin films as a function of the DIO concentration. The 2D GIWAXS data of printed thin film based on PBDB-T-SF:IT-4F (Figure S4) show an increase in intensity with rising DIO concentration for the (010) and (100) PBDB-T-SF Bragg peak signals and for the (100) IT-4F Bragg peak signal.⁵⁴ In addition, higher order Bragg peaks become visible in the 2D GIWAXS data, indicating an overall increase in crystallinity with increasing DIO concentration. The increase in crystallinity originates from reduced intermolecular interactions allowing the molecules to move freely, rearrange, and form more crystalline structures. For a thin film printed with a 1:1 weight ratio of PBDB-T-SF and IT-4F with different DIO concentrations, the azimuthal q integral and tube cuts of the strongest (100) Bragg peaks from the 2D GIWAXS data are shown in Figure 3.

The (100) PBDB-T-SF ($2.2 < q < 2.6 \text{ nm}^{-1}$) and the (100) IT-4F (2.65 < q < 2.9 nm⁻¹) peak orientation distributions are analyzed by fitting of Gaussian functions (Figure 3b,c). For both the polymer and the small molecule acceptor, the (100) signal can be assigned to an edge-on orientation of the crystallites. The FWHM of the Gaussian fits to the (100) PBDB-T-SF peak orientation distribution broadens from (4.7 \pm 0.2) ° for 0.00 vol % DIO to (27.2 \pm 0.6)° for 0.25 vol %, $(33.7 \pm 2.5)^{\circ}$ for 0.50 vol %, and $(38.1 \pm 2.5)^{\circ}$ for 1.0 vol % DIO. For the (100) IT-4F peak, the FWHM increases from $(12.8 \pm 0.9)^{\circ}$ to $(16.4 \pm 2.2)^{\circ}$ for 0.25 vol %, $(17.3 \pm 0.6)^{\circ}$ for 0.5 vol %, and $(18.6 \pm 1.3)^{\circ}$ for 1.0 vol % DIO. Such broadening in the orientation distribution indicates an enhanced rotational disorder of crystallites in the thin film with rising DIO concentration. As an edge-on orientation facilitates the charge transport parallel to the substrate and respectively parallel to the electrodes, the present orientation has an unfavorable effect on the solar cell performance. 45,55-57

For comparison, the 2D GIWAXS data (Figure S5), azimuthal q integrals, and tube cuts (Figure S6) of printed pure IT-4F and pure PBDB-T-SF films with 0.25 vol % DIO are shown. We observe a similar crystallization behavior for the pure polymer in absence of an acceptor whereas the pure IT-4F film shows lower crystallinity but more ordered structures. Polymer–acceptor interactions seem to have a positive effect on the crystallization of IT-4F but enhance the rotational disorder of crystallites.

Thus, the results from X-ray scattering experiments and SEM show the significant impact of the DIO concentration on the morphology and expected solar cell performance of printed active layers based on a 1:1 blend of PBDB-T-SF:IT-4F.

2.2. Optical Properties of Active Layers and Printed Organic Solar Cells. PL is measured for thin films of the pure electron polymer PBDB-T-SF, the pure acceptor IT-4F, and a blend of 1:1 of donor and acceptor after excitation with a wavelength of 570 nm (Figure 4a).



Figure 4. (a) PL of the pure donor polymer PBDB-T-SF, the pure nonfullerene acceptor IT-4F, and an active layer printed with a 1:1 ratio of donor and acceptor out of chlorobenzene; (b) PL of active layers printed with varying DIO concentrations.

The pure materials show high PL intensity, whereas in a blend of PBDB-T-SF:IT-4F the electron transfer from donor to acceptor provokes a significant reduction in intensity. As the low-bandgap polymer PBDB-T-SF shows absorbance in a broad wavelength range in the region of visible light (Figure 5), it can be efficiently excited with the chosen wavelength. In a



Figure 5. UV/vis absorbance spectra of active layers of PBDB-T-SF:IT-4F (1:1) printed out of chlorobenzene with different DIO concentrations normalized on the dry film thickness.

BHJ organic solar cell, the mechanism of energy conversion starts with excitation of the polymer by absorption of a photon and generation of an exciton.^{58,59} During the exciton lifetime, the electron and electron hole, being attracted to each other by Coulomb forces move toward the interface where the exciton splitting in a positive and a negative charge occurs. The electron is transferred to the electron acceptor (IT-4F) whereas the electron hole remains at the conjugated polymer. In a last step, the electron and the electron hole are transported toward the respective electrodes where the current can be extracted.



Figure 6. (a) EQE spectra and (b) integrated photocurrent density of printed organic solar cells based on PBDB-T-SF:IT-4F with different DIO concentrations.

In absence of an acceptor, the polymer undergoes a transition back to the electronic ground state after the excited state lifetime under emission of a photon (PL).⁶⁰ The electron transfer from donor to acceptor provokes a reduction in PL intensity and allows us to draw conclusions about the efficiency of the charge transfer in an organic solar cell.^{53,61,62} PL of printed active layers with different DIO concentrations is measured after excitation with a wavelength of 570 nm (Figure 4b). Increasing DIO concentration causes a decrease in luminescence intensity. Due to decreasing domain sizes with increasing DIO concentration (Figure 1b), the interface area grows and charge transfer from the donor polymer to the acceptor molecule is facilitated. In addition, the exciton is generated closer to the interface and the distance which needs to be overcome by exciton diffusion is reduced. This has a significant impact on the performance of BHJ organic solar cells as typical exciton diffusion lengths are about 10 nm.^{59,63} The loss mechanism of charge recombination before reaching the interface becomes less probable. A moderate increase in distance between donor and acceptor can improve the solar cell performance by reduction of Coulomb forces and charge stabilization.^{15,52} In this case, exciton splitting is facilitated and the probability of charge recombination at the interface is reduced. These effects cause a decrease in photoluminescence intensity with rising DIO concentrations (Figure 4b). To conclude, the addition of higher solvent additive concentrations and the resulting small average domain sizes facilitate the charge transfer from donor to acceptor by an enlargement of interface area but can provoke a decline in the PCE by charge trapping.5

To study the influence of DIO on the absorption properties of printed BHJ organic solar cells, UV/vis spectroscopy is performed (Figure 5).

The resulting absorbance spectra are normalized on the film thicknesses. The active layer based on a 1:1 blend of PBDB-T-SF:IT-4F shows absorbance in a broad wavelength range of visible light. The optical bandgap of the active material is determined with the Tauc plot method (Figure S7) to be (1.55 \pm 0.04) eV. The addition of DIO does not shift the bandgap itself but significantly influences the absorbance of photons with energies slightly above it due to increased crystallinity in the active layer.⁶⁴ An optimum DIO concentration of 0.25 vol % improves the absorbance in the wavelength range from 700 to 800 nm as compared to solvent additive free thin films. Active layers processed with higher concentrations of DIO (0.50 vol % and 1.0 vol %) show a distinct reduction of

absorbance in this wavelength range with rising amounts of solvent additive due to an increased rotational disorder in the thin films.⁶⁵ By addition of low DIO concentrations (0.25 and 0.50 vol %), active layers of PBDB-T-SF:IT-4F show an enhanced absorbance in the wavelength range from 570 to 700 nm. The best absorption spectra is obtained for a DIO concentration of 0.25 vol % as the absorbance is significantly increased over a broad wavelength range (570–800 nm), which enables us to exploit the sun spectra more efficiently. The probability for generating photocurrent after absorption of a photon with a certain wavelength is studied with EQE. The EQE spectra and the integrated current density of printed organic solar cells with different DIO concentrations are shown in Figure 6.

In the wavelength range from 300 to 520 nm the device printed with a DIO concentration of 0.25 vol % shows a considerably lower EQE (Figure 6a) and absorbance (Figure 5) compared to devices with 0.00, 0.50, and 1.0 vol % DIO and a lower integrated current density can be observed between 300 and 610 nm (Figure 6b). Between 300 and 520 nm, the addition of DIO seems to have a negative effect on the device performance as the solar cell printed without solvent additive shows a significantly higher EQE compared to devices with DIO (Figure 6a). However, in the wavelength range between 570 and 780 nm, a significantly enhanced EQE can be observed for a DIO concentration of 0.25 vol % (Figure 6a). This is in accordance with the distinct increase of absorbance in this wavelength range (Figure 5). In the wavelength range above 610 nm, the integrated photocurrent of the solar cell printed with a DIO concentration of 0.25 vol % clearly exceeds that of solar cells with other DIO concentrations. The addition of an optimum solvent additive concentration of 0.25 vol % seems to provoke the formation of a morphology favorable for the absorbance of low energy photons and subsequent photocurrent generation.

2.3. Device Performance of Printed Organic Solar Cells. Printed organic solar cells based on PBDB-T-SF:IT-4F (Figure S2b) are fabricated with different concentrations of DIO with a solar cell area about 6.25 cm² and a pixel size of 0.12 cm^2 . For each DIO concentration, three times eight solar cells are tested. The resulting PCE values are shown in Figure 7.

Slot-die coated organic solar cells without DIO reach an average PCE of (3.5 ± 0.8) %. The addition of 0.25 vol % DIO to the precursor solution improved the average PCE to (7.9 ± 0.7) % with a top device performance of 8.95%. The



Figure 7. PCE of organic solar cells printed with different DIO concentrations. Efficiencies of measured pixels (small colored dots), the average device performance (red square) and the standard deviation (gray error bar) are given for different solvent additive concentrations.

corresponding short circuit density (J_{SC}) of 19.46 mA/cm² and the open-circuit voltage (V_{OC}) of 0.87 V are close to literature values for spin-coated small area devices with 0.5 vol % DIO (Jsc = 20.88 mA/cm² and Voc = 0.88 V for an aperture area of 0.037 cm² or JSC = 18.93 mA/cm² and V_{OC} = 0.86 V for an aperture area of 1 cm²).¹⁹ The deviation in optimum DIO concentration in printed devices compared to spin-coated devices originates from different polymer and acceptor concentrations used for printing (7 mg/mL for printing vs 20 mg/mL for spin-coating) giving a different DIO to active material ratio. By further increasing the DIO concentration, average PCE values of (4.6 ± 0.3) % for 0.50 vol % and (4.6 ± 0.9) % for 1.0 vol % of DIO are obtained (Table 1).

Table 1. Best PCE Values for Slot-Die Coated Organic SolarCells with Different DIO Concentrations and theResponsive Short Circuit Current Density, Open-CircuitVoltage and Fill Factor^a

DIO concentration [vol %]	best PCE [%]	$J_{\rm sc}$ [mA/cm ²]	$V_{\rm OC}$ [V]	FF [-]	average PCE [%]
0.00	4.80	14.18	0.86	0.39	3.5 ± 0.8
0.25	8.95	19.46	0.87	0.52	7.9 ± 0.7
0.50	5.17	14.19	0.82	0.44	4.6 ± 0.3
1.0	4.98	13.32	0.85	0.44	4.6 ± 0.9
^{<i>a</i>} For all solvent additive concentrations, average PCE values are given.					

At an optimum DIO concentration of 0.25 vol %, the short circuit density of the slot-die coated organic solar cells is significantly enhanced as smaller structures are formed. The interface area between donor and acceptor increases and exciton splitting is facilitated. At higher DIO concentrations, a smaller J_{SC} is observed due to charge trapping provoked by very small structures in combination with large distances. In addition, DIO enhances the crystallinity of IT-4F and PBDB-T-SF and influences the V_{OC}. At an optimum solvent additive concentration of 0.25 vol %, the $V_{\rm OC}$ is slightly enhanced due to higher crystallinity. Due to edge-on orientation of the crystallites, charge transport occurs parallel to the electrodes which is not favorable for the device performance. For a DIO concentration of 0.50 and 1.0 vol %, this effect is further enhanced and a lower V_{OC} is observed. Current-voltage curves for best devices processed with varying DIO concentrations are shown in Figure 8.



Figure 8. Current-voltage curves for the best photovoltaic devices printed out of chlorobenzene with different DIO concentrations.

Organic solar cells processed with 0.25 vol % DIO exhibit the best performance as the solvent additive simultaneously has positive and negative effects on the morphology and optical properties. For a small DIO concentration of 0.25 vol %, the positive effects such as an increased crystallinity and gain of interface area by decreasing average structure sizes dominate whereas at higher DIO concentrations, the negative effects such as an increased rotational disorder of crystallites and loss mechanisms due to large distances between domains dominate. The average PCE improved significantly by addition of an optimum DIO concentration of 0.25 vol % compared to solvent additive free devices whereas at higher concentrations the positive effect on the solar cell performance is less pronounced.

These findings are fully consistent with the morphology and optical properties obtained with GISAXS, GIWAXS, SEM, AFM, PL, UV/vis spectroscopy and EQE and demonstrate the significant influence of the DIO concentration on the structure and performance of printed high-efficiency organic solar cells.

3. CONCLUSIONS

We have investigated the effect of DIO on the morphology, optical properties and power conversion efficiency of printed BHJ organic solar cells based on the conjugated polymer PBDB-T-SF and the small molecule acceptor IT-4F. A slot-die coater has been used for the thin film deposition of the active material. Scattering experiments in grazing incidence geometry as well as SEM and AFM reveal shrinking average structure sizes and growing distances between the domains with rising DIO concentration. Moreover, the crystallinity is enhanced by addition of DIO, which appears beneficial as higher crystallinity typically causes better device performance. However, due to an edge-on orientation of the crystallites, charge transport parallel to the electrodes is facilitated, which is less favorable for the solar cell performance. A decrease in PL intensity with rising DIO concentration shows an improved charge transfer from the polymer donor to the small molecule acceptor due to reduced average domain sizes and an enlargement of the interface area. UV/vis spectroscopy and EQE show an improved absorbance and facilitated generation of photocurrent for a DIO concentration of 0.25 vol % in a broad wavelength range. An optimum DIO concentration of 0.25 vol % yields the best photovoltaic performance. Thus, a different amount of DIO (0.25 vol %) is giving optimal devices as compared to spin-coating (0.5 vol %). The average PCE of these printed devices improves from 3.5 to 7.9% compared to devices processed without solvent additive and efficiencies up to 8.95% are obtained. At higher DIO concentrations, the PCE cannot be further improved due to the formation of small

average structure sizes, which provoke charge trapping. Thus, similarly as for spin-coated active layers also in case of printed active layers, the morphology optimization is important for achieving best performing solar cells and parameters optimized for spin-coating cannot be simply transferred to printing. The present results are an important step toward a further upscaling of high-efficiency organic solar cells.

4. EXPERIMENTAL SECTION

4.1. Device Fabrication. Poly[(2,6-(4,8-bis(5-(2-ethylhexylthio)-4-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PBDB-T-SF, Solarmer) and 3,9-bis(2methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno-[1,2-b:5,6-b']dithiophene (IT-4F, Solarmer) were dissolved in chlorobenzene (Merck) to get a 7 mg/mL solution and stirred for 48 h at 100 °C. Appropriate volumes of 1,8-diiodooctane (DIO, Carl Roth GmbH) were added to the solution before printing. Microscope slides (7.5 cm \times 2.5 cm) purchased from Carl Roth GmbH were used as substrates for printing of active layers and postcharacterized with GISAXS, SEM, PL and UV/vis spectroscopy. The glass substrates were cleaned in a mixture of 50 mL deionized H₂O, 80 mL H₂O₂ (Carl Roth GmbH) and 180 mL H_2SO_4 (Carl Roth GmbH) for 15 min at 80 °C. After rinsing with deionized water and drying with N_{22} the glass substrates were O2-plasma treated for 10 min (Plasma-System-Nano, Diener Electronic GmbH, 0.4 mbar, 83% power). Slotdie coating was performed at room temperature. Resulting film thicknesses were about 100 nm. For fabrication of organic solar cells with inverted geometry (glass/ITO/BHJ/MoO₃,Al), indium tin oxide (ITO) coated glass substrates (7.5 cm \times 2.5 cm) with a sheet resistance of 12 ohms/sq were purchased from SOLEMS. After ultrasonic cleaning with Alconox (Merck), deionized water, acetone (Merck) and isopropanol (Merck) sequentially for 20 min, the substrates were plasma treated. A precursor solution consisting of 1 g zinc acetate dihydrate (Merck) in 10 mL 2-methoxyethanol (Merck) and 284 μ L ethanolamine (Merck) was spin-coated (5000 rpm, 60s) on the ITO-coated glass substrates and annealed at 200 °C for 60 min in air. After cooling down to room temperature, the active layer was printed at room temperature. Ten nm layers of MoO3 (Carl Roth GmbH) and 100 nm layers of Al (chemPUR) were thermally evaporated on top of the printed active layer under vacuum (10mbar).

4.2. Scattering Experiment. Scattering experiments were performed with a Ganesha SAXSLAB instrument and at the MiNaXS beamline P03 (DESY, Hamburg).⁶⁶ Details of the scattering experiments are reported in the Supporting Information. Data analysis was performed with the programs DPDAK (Directly Programmable Data Analysis Kit)⁶⁷ and GIXSGUI.⁶⁸

4.3. Surface Morphology. The surface morphology was probed with scanning electron microscopy (SEM) and atomic force microscopy (AFM) and experimental details are provided in the Supporting Information.

4.4. Optical Characterization. Photoluminescence (PL) was measured with a PerkinElmer Fluorescence spectrometer LS 55. For the measurement, an excitation wavelength of 570 nm was used. PL was detected from 600 to 900 nm. For clarity, regions with negligible PL intensity (600–749 nm and 851–900 nm) were not shown. The absorbance spectra were measured with a PerkinElmer UV/vis spectrometer Lambda 650S. All spectra were normalized on the film thickness.

External quantum efficiency (EQE) spectra were measured using a Oriel QE–PV-SI Quantum Efficiency Measurement Kit provided from Newport. The photocurrent generated at different wavelengths was measured under illumination with a 6258 Xe OF lamp (Newport, 300 W), set with a reference and corrected for spectral error⁶⁹ to fulfill standard test condition requirements (AM 1.5 illumination, 100 mW/ cm²). All solar cells (2.5 cm \times 2.5 cm, 0.12 cm² pixel size) were measured at ambient conditions without encapsulation.

4.5. Film Thickness. The film thickness values of all films were determined with a BRUKER DektakXT profilometer.

4.6. IV Characterization. Current–voltages curves were measured under AM1.5 illumination (100 mW/cm²) with a SourceMeter Keithley 2400 at ambient conditions without encapsulation. The solar cell area was 2.5 cm \times 2.5 cm with a pixel size of 0.12 cm².

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b16784.

Experimental details, thin film deposition, and photograph of printed active layer and solar cell, GISAXS measurements, GIWAXS measurements, and Tauc plot (PDF)

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Notes

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