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Abstract
To tailor the nanomorphology in polymer/fullerene blends, we study the effect of electrostatic field (E-field) on the solidification of poly(3-hexylthiophene-2, 5-diyl) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PC60BM) bulk heterojunction (BHJ). In addition to control; wet P3HT:PC60BM thin films were exposed to E-field of Van de Graaff (VDG) generator at three different directions—horizontal (H), tilted (T), and vertical (V)—relative to the plane of the substrate. Surface and bulk characterizations of the field-treated BHJs affirmed that fullerene molecules can easily penetrate the spaghetti-like P3HT and move up and down following the E-field. Using E-field treatment, we achieved favorable morphologies with efficient charge separation, transport, and collection. We improve; (1) the hole mobility values up to $19.4 \times 10^{-4} \pm 1.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and (2) the power conversion efficiency (PCE) of conventional and inverted OPVs up to $2.58 \pm 0.02\%$ and $4.1 \pm 0.40\%$, respectively. This E-field approach can serve as a new morphology-tuning technique, which is generally applicable to other polymer–fullerene systems.

Keywords
electrostatic field, fullerene, nanomorphology, P3HT, Van de Graaff OPVs

Disciplines
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Tailoring Nanoscale Morphology of Polymer: Fullerene Blends Using Electrostatic Field

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KEYWORDS: P3HT, fullerene, nanomorphology, electrostatic field, Van de Graaff, OPVs
ABSTRACT

To tailor the nanomorphology in polymer/fullerene blends, we study the effect of electrostatic field (E-field) on the solidification of poly(3-hexylthiophene-2, 5-diyl) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PC$_{60}$BM) bulk heterojunction (BHJ). In addition to control; wet P3HT:PC$_{60}$BM thin films were exposed to E-field of Van de Graaff (VDG) generator at three different directions – horizontal (H), tilted (T) and vertical (V) – relative to the plane of the substrate. Surface and bulk characterizations of the field-treated BHJs affirmed that fullerene molecules can easily penetrate the spaghetti-like P3HT and move up and down following the E-field. Using E-field treatment, favorable morphologies with efficient charge separation, transport, and collection were achieved. We improve; (1) the hole mobility values up to $19.4 \times 10^{-4} \pm 1.6 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ and (2) the power conversion efficiency (PCE) of conventional and inverted OPVs up to $2.58 \pm 0.02\%$ and $4.1 \pm 0.40\%$, respectively. This E-field approach can serve as a new morphology-tuning technique, which is generally applicable to other polymer-fullerene systems.
Introduction

During the past decade solution-processed organic photovoltaic (OPVs) have been witnessing a tremendous interest because of their promising properties including light-weight, mechanical flexibility, and large area roll-to-roll manufacturing.\textsuperscript{1-3} Power conversion efficiencies (PCE) exceeding 11% have been reported for single-junction\textsuperscript{4} and multijunction\textsuperscript{5-6} OPVs. Achieving high PCE is primarily due to different routes: (1) synthesis and development of new photovoltaic materials,\textsuperscript{7} (2) proper selection of devices’ configuration including cathodic and anodic layers,\textsuperscript{8} (3) increasing the light absorption inside the photoactive layer via optical\textsuperscript{9-10} and ferroelectric\textsuperscript{11} approaches, and (4) optimization of nanoscale morphology in polymer/fullerene bulk heterojunction (BHJ).\textsuperscript{12} Among the aforementioned routes, morphology-tuning techniques (such as thermal annealing,\textsuperscript{13-16} solvent annealing,\textsuperscript{17-18} slow growth,\textsuperscript{19-20} and using low-vapor-pressure solvents\textsuperscript{21} and solvent used)\textsuperscript{22-24} have been extensively explored. Typically, these techniques improve polymer crystallinity, or affect phase separation in donor-acceptor BHJ, or both that influence the efficiency and stability of organic solar cells.\textsuperscript{25-26} However, the applicability and optimization of these techniques are material specific; for instance, thermal annealing improves structural order in classic polythiophenes, but worsens it in a recent high efficiency polymer system.\textsuperscript{27} Electrostatic field (E-field) has been used to align inorganic nanowires,\textsuperscript{28} control the growth and orientation of pentacene single crystals,\textsuperscript{29} align liquid crystals in ternary photovoltaic blends,\textsuperscript{30} and control morphology in polymer-based thin films.\textsuperscript{31-32} However, the effects of E-field on the properties of polymer/fullerene thin films and devices are not well understood. Thus far, there are only two conflicting reports; one\textsuperscript{33} shows that E-field parallel to the substrate improves photovoltaic device performance and perpendicular field has no effect, whereas the second\textsuperscript{34} shows that perpendicular field improves the device performance.
In this work, we report the influence of solidifying poly(3-hexylthiophene-2, 5-diy1):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PC60BM) thin films in E-field of a Van de Graaff generator (VDG). Immediately after their spin-coating on indium-doped tin oxide (ITO) substrates, wet P3HT:PCBM thin films were exposed to the E-field of VDG at different directions: Horizontal (H), tilted (T) and vertical (V). We studied the effect of E-field on the morphology of P3HT:PCBM thin films using Kelvin probe force microscopy (KPFM), grazing incidence wide-angle X-ray scattering (GIWAXS) measurements and photoluminescence (PL) spectroscopy, and investigated the correlation between morphology and electrical properties such as carrier mobility and power conversion efficiency (PCE) in polymer/fullerene thin films and devices.

**Materials and Methods**

**Description of Van de Graaff generator**: A Van de Graaff generator, which can produce an electric potential of 325,000 volts or more, was utilized to produce an E-field of ~5.8 kV/m at the VDG’s surface. The ITO-coated active layers were aligned 1 cm from the dome surface, where the E-field strength was calculated to be ~5 kV/m. **Figure 1a** shows real image of the VDG dome surrounded by three petri dishes (red arrows show the direction of E-field lines).

**Substrate preparation**: Indium tin oxide (ITO) coated glass slides (5-15 Ω/□, Delta Technologies) were ultrasonicated in detergent, de-ionized water, methanol/ethanol and 2-propanol. The substrates were dried with nitrogen and on a hot plate at 150°C for 5 minutes before receiving a medium dose of air plasma treatment for 5 minutes. The ITO slides were blown again with N2 gas before any depositions.
**OPVs fabrication:** 40 nm of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (VP 4083, HC Stark) was spin coated at 4000 rpm for 60 seconds on cleaned ITO, and then annealed at 150°C for 30 minutes. The P3HT:PC$_{60}$BM (1:1, w/w; 20 mg/mL; 1-Material) was dissolved in ortho-dichlorobenzene by stirring overnight at 850 rpm on a hot plate at 50°C. The P3HT:PC$_{60}$BM solution was filtered with a plastic syringe and 0.2 µm filter before spincoating at 500 rpm/40s on ITO. In addition to control, P3HT:PC$_{60}$BM-coated substrates were exposed to E-field of VDG at directions shown in Figure 1a until they dried completely. Ca and Al were thermally evaporated in 10$^{-6}$ mbar vacuum at rates of 1 and 4 Å/s, respectively. The device had a structure of ITO/PEDOT:PSS/active-layer/ Ca (20 nm)/Al (100 nm). PEDOT:PSS and Ca were replaced by Cs$_2$CO$_3$ and MoO$_x$ to yield inverted OPVs [structure: ITO/ Cs$_2$CO$_3$/P3HT:PC$_{60}$BM/ MoO$_x$ (10 nm)/ (100 nm) Al]. The concentration and the spin speed conditions were kept the same in both conventional and inverted OPVs. More than 100 devices, each of area of 0.1256 cm$^2$, were fabricated under E-field treatment. The current-voltage characteristics were measured using an ELH Quartzline halogen lamp calibrated at 1 sun. PL lifetime measurement was investigated by the time-correlated single-photon counting setup at a probing fluorescence wavelength of 400 nm.$^{35}$ PARSTAT 2273 was utilized with a solar simulator to measure $V_{oc}$ versus light intensity dependence. A Keithley 2400 source/meter was used to measure mobility of P3HT:PC$_{60}$BM devices.

**GIWAXS measurements:** Samples for GIWAXS were spin-coated at 500 rpm/40 seconds on 1-inch × 1-inch bare silicon wafers. GIWAXS measurements were carried out at the Beamline 8-ID-E of the Advanced Photon Source, Argonne National Lab.$^{36}$ X-rays with photon energy of 7.35 keV were incident upon the sample at angles $\alpha_i$ of 0.15°, below the critical angle for the organic thin film, or 0.2°, above the critical angle of the thin film but below the critical angle of
the Si substrate, in order to probe the region near the top surface of the film, or to probe the entire thickness of the thin film, respectively. For P3HT, chemical formula \((\text{C}_{10}\text{H}_{14}\text{S})_n\), mass density 1.1 g/cm\(^3\), corresponds to an electron density 0.359 e/A\(^3\). At E=7.35 keV, the critical angle is \(\alpha_x = 0.1735^\circ\). The beam size was defined by slits 200 µm horizontally and 20 µm vertically, so the x-ray footprint along the beam extended to about 7.6 mm for the smaller incident angle. Samples were enclosed in a chamber purged with helium gas to minimize concerns about radiation damage. A mica entrance window and an internal beamstop before the kapton exit window of the chamber minimized parasitic scattering from the chamber. Two-dimensional data were obtained with a Pilatus 1M detector (Dectris) at two different vertical positions, and the images were combined to eliminate rows of inactive pixels using the software package GIXSGUI for Matlab (Mathworks). \(^{37}\) This also applied corrections for detector non-uniformity, pixel sensitivity, geometry and polarization, and mapped the data from pixel-space to the photon wave-vector transfer vector, \(q\). All the 2-D data shown were collected for the same exposure time and are displayed on the same pseudocolor intensity scale. The intensity of the data along the polar angle in this representation, \(\chi\), describes a partial pole figure. From the linecuts of \((100)\) peak, we calculated the FWHM using Gaussian function in OriginLab software.

**Kelvin probe force microscopy imaging**: Kelvin probe force microscopy was performed using Agilent 5500 SPM in single pass and frequency modulation mode. NANOSENSORS PtSi-NCH probe was used for all samples. Two lock-in amplifiers were utilized where the first lock-in amplifier was used to track the topography. The AFM tip was vibrated close to its first mechanical resonance using lock-in amplifier 1 (LIA1) which was used to track the topography and phase. Lock-in amplifier 2 (LIA2) was used to apply AC excitation to the conductive tip at 4kHz frequency and dc bias of -0.5V. The Y component of LIA1 was fed as input for LIA2. The
phase shift of both LIA1 and LIA2 were adjusted to maximize the X component and minimize the Y component of each lock in amplifier to obtain an optimum signal to noise ratio. Both topography and surface potential were tracked simultaneously. All the images were analyzed using Nanotec Electronica WSxM software.

Figure 1. (a) Photograph of the Van de Graff generator (VDG) showing the directions (horizontal, tilted and vertical) of E-field applied to our films. The effect of E-field on (b-d) P3HT (concentration: 10mg/ml in ortho-dichlorobenzene) and pure dichlorobenzene drops, and (e-g) PC$_{60}$BM drop (concentration: 10mg/ml in ortho-dichlorobenzene). Black arrows in Figure 1b and e point to the place of drops on glass slide placed in front of VDG sphere. Red ellipse shown in Figure 1f shows the flight of fullerene molecules toward VDG sphere.

Results and discussion

First, to inspect the effect of E-field on conjugated polymers and fullerenes, three droplets were placed near the hollow metal sphere of VDG (Figure 1b-g). The first droplet, which is a neat drop of non-polar ortho-dichlorobenzene, showed no response to E-field (Figure 1b-d and Video S1). In contrast, P3HT and PC$_{60}$BM dissolved in ortho-dichlorobenzene were pulled towards the VDG dome and completely left the glass slide in ~50 seconds and ~3 seconds (Figure 1b-g and Video S1 and S2), respectively. The quicker response of the PCBM droplet...
can be ascribed to: (1) the small size of PCBM molecules in comparison to the long intertwined P3HT polymer chains, and (2) the permanent dipole moment of PCBM molecules.\textsuperscript{39-40} We also observed that E-field similarly pulled droplets of P3HT:PCBM solution as well as other polymers, such as poly[[9-(1-octynonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT). We speculated from this observation that the E-field can impact the solidification behavior of P3HT:PCBM thin films and tailoring the nanoscale phase distribution in BHJ. Thereby, we next probed the surface phase distribution in P3HT/PCBM thin films using Kelvin probe force microscopy (KPFM).

\textbf{Figure 2a-d} shows typical surface potential (SP) maps in P3HT-PCBM samples. These SP maps were quantitatively analyzed by the histograms shown in \textbf{Figure 2e-h}. The SP map of the control (untreated P3HT:PCBM films) displays both fine and coarse P3HT aggregates (in red) and PCBM clusters (in blue) (see black arrows in \textbf{Figure 2a}), which agrees with previous work on the same polymer/fullerene system.\textsuperscript{41} The histogram in \textbf{Figure 2e} of the SP map of the control displayed broad distribution of P3HT and PCBM domains with grain sizes exceeding \textasciitilde200 nm in length. The vertical line located at \textasciitilde310 mV, which crosses all SP histograms in \textbf{Figure 2e-h}, is to show the deviation in SP distribution relative to the control case. The H-film (i.e., thin film treated with horizontal E-field) exhibited narrow SP distribution (\textbf{Figure 2f}) with refined nanomorphology, displaying slight increase in PCBM signal and less P3HT contribution. Remarkably, applying E-field in T-direction significantly pulled more PCBM molecules (more bluish color in \textbf{Figure 2c}) upward towards the E-field and barely showed P3HT nanoclusters with grain sizes of \textasciitilde50 nm. This conclusion is assured by the histogram shown in \textbf{Figure 2g} and \textbf{S1b}. This histogram is obviously shifted to lower SP values (center at \textasciitilde255 mV). Conversely, the opposite scenario occurred in KPFM map of V-films (i.e., thin film treated with vertical E-
Vertical E-field attracted fullerene molecules downward, leaving large P3HT aggregates (more reddish color in Figure 2d) on the surface. Consequently, SP histogram of vertical KPFM maps is significantly shifted to the right with SP distribution centered at ~382 mV (Figure 2h and supporting information Figure S1b). Remarkably, our KPFM findings are confirmed by the elemental analysis conducted by x-ray photoelectron spectroscopy (XPS) as tabulated in Table S1. Considering all of these scenarios, we concluded that; the small fullerenes are more mobile than “spaghetti-like” P3HT; they can easily penetrate the polymer network and follow the E-field, leading to significant changes in nanoscale morphology of P3HT:PCBM BHJs.

Figure 2. (a-d) Surface-potential maps and (e-h) KPFM histograms of solution-processed P3HT:PC_{60}BM thin films. All the KPFM maps (scan size: 1.5 μm x 1.5 μm) were captured at bias of -0.5 volts in dark, and analyzed using WxSM software^{38}. Black arrows show P3HT (in red) and PCBM (in blue) aggregates. Surface potential histograms of control, horizontal, tiled
and vertical KPFM maps are centered at 310, 288, 255 and 382 mV, respectively. In Figure 2e-h, the vertical line located at ~295 mV crossing all SP histograms is to show the center of surface potential distribution of the control KPFM map.

To further investigate how the E-field treatment affects the bulk of polymer/fullerene blend, we performed grazing incidence wide-angle X-ray scattering (GIWAXS) measurements. Figure 3 shows two-dimensional GIWAXS images of P3HT:PCBM thin films. P3HT is known to have edge-on, face-on or mixed conformations depending on processing conditions. In our measurements, the film surface was selectively probed using 0.15° incident angle (below the polymer critical angle), and the bulk was probed using 0.2° angle (above polymer critical angle). All P3HT:PCBM films display out-of-plane (100), (200), and (300) lamellar stacking peaks (along $q_r = 0 \text{ Å}^{-1}$) and an in-plane (010) $\pi-\pi$ stacking peak (at around $q = 1.65 \text{ Å}^{-1}$) that indicates the edge-on conformation of P3HT (Figure 3a-h). Linecuts of the (100) peak ($0.35 < q < 0.45 \text{ Å}^{-1}$) (check the supporting information Figure S2a) showing the intensity versus polar angle in the detector plane in the $q_r$ vs. $q_z$ plane, $\chi$, for the 0.15° incident angle case display FWHM of $17.8 \pm 0.48°$, $18.4 \pm 0.49°$, $17.6 \pm 0.10°$ and $12 \pm 0.09°$ for the control, H-, T- and V-films, respectively. Lower FWHM indicates an increased edge-on conformation (i.e., side-chains are perpendicular to the plane of the substrate) and decreased mosaicity. Films exposed to vertical E-field showed diminished PCBM ring for incident angle of 0.15° (see yellow arrow in Figure 3d), implying that vertical E-field depletes PCBM molecules from the film surface. This result agrees with the SP histogram results of the KPFM maps in the vertical case (see Figure 2d and h), in which the surface of P3HT-PCBM film is completely covered with P3HT aggregates. Higher concentration of PCBM away from the surface is further affirmed by probing the bulk of the film. At grazing incident angle of 0.2°, Figure 3e-h, all films show significantly higher X-ray
scattering than the surface spectra. The GIWAXS map of the films exposed to vertical E-field reveals an intense fullerene ring, assuring that PCBM molecules migrate to the substrate/blend interface. Considering the smaller size of PCBM molecules and their quicker attraction to E-field in the droplet experiment (Figure 1b-g, Video S1 and S2), it is not surprising that vertical E-field pulls fullerene molecules down away from the surface. Again, linecuts shown in Figure S2b of the (100) peak display reduced FWHM of 20.1 ± 0.16° for films exposed to vertical E-field compared to the control (25.8 ± 0.19°), horizontal (26 ± 0.24°) and tilted (25.7 ± 0.83°) cases. Our published work on fluorescence and Raman measurements affirms our GIWAXS results that the static forces of E-field induce anisotropic orientation in P3HT-only thin films. So far, we showed that E-field plays critical role in tailoring the surface morphology and phase distribution in P3HT-PCBM BHJ. Table S2 shows the best-fit parameters obtained from the I(q_z) curves (Figure S3) for the center and full width at half maximum (FWHM) obtained for the (100) peaks. For the d-spacing and coherence length, we concluded that the E-filed does not affect d-spacing and coherence length much. However, integration of the sine-weighted I(χ) curves (shown in Figure S4) shows that they are consistent with an enhancement in the crystallinity of the vertically applied E-field samples by about 15% relative to the samples prepared with horizontal E-field or no E-field (as tabulated in Table S3). We believe that 15% change in crystallinity could make a big change in terms of percolation pathways for charge transport.
**Figure 3.** Two-dimensional GIWAXS patterns of P3HT:PC<sub>60</sub>BM thin films at grazing incidence angles of (a-d) 0.15° and (e-h) 0.2°.

To probe the efficiency of exciton quenching and determine the degree of polymer/fullerene intermixing in BHJs, we investigated photoluminescence (PL) spectroscopy measurements for E-field-treated and untreated P3HT:PCBM films using time-correlated single-photon counting (TCSPC) technique.\textsuperscript{35} In **Figure 4a**, the P3HT:PCBM film processed in vertical E-field exhibited an obvious increase in PL decay relative to the other films. This PL increase corresponds to significant radiative recombination of excitons generated within the polymer aggregates, which have domain sizes exceeding the exciton diffusion length (i.e., about 5 to 10 nm).\textsuperscript{50-51} Fitting of the PL spectra revealed bi-exponential decay with two lifetimes (i.e., τ<sub>1</sub> and τ<sub>2</sub>)\textsuperscript{52-53} (**Figure 4a**, inset), which agrees with previous work.\textsuperscript{54} The difference in τ<sub>1</sub> for the untreated films (52 ± 0.5 ps) and films processed in H- (49 ± 0.4 ps) and T-field (51 ± 0.5 ps) are insignificant compared to those films processed in V-field (93 ± 1.3 ps). Conversely; while the τ<sub>2</sub> lifetime values for the H- (441 ± 23 ps) and T-films (405 ± 19 ps) are higher than the control film (378 ± 18 ps), the V-
films exhibits significant increase in the $\tau_2$ value ($624 \pm 17$ ps). This increased $\tau_2$ value of V-film, which is close to that reported for neat P3HT thin films (660 ps),\textsuperscript{55} is strong sign of increased demixing between P3HT and PCBM phases and is attributed to increased emissive states in P3HT thin films.\textsuperscript{52} This demixing enhances the charge transport within P3HT crystalline-domains and in-between them; however, poor exciton dissociation occurs when the grain sizes exceed the exciton diffusion length. The connectivity between P3HT crystalline-domains plays a vital role in determining the efficiency of carrier transport.\textsuperscript{49}

We next determined the hole mobilities in P3HT:PCBM hole-only devices by the space charge limited current (SCLC) measurements. In Figure 4b, the current-voltage curve of hole-only devices fabricated in H- and T-fields exhibited higher current values than control and devices exposed to V-field. The hole mobility of the control film is $8.93 \times 10^{-4} \pm 0.2 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ (average hole mobility ± standard deviation). Exposing P3HT:PCBM thin films to H-, T-, and V-fields improves the hole mobility to $19.4 \times 10^{-4} \pm 1.6 \times 10^{-4}$, $18.4 \times 10^{-4} \pm 3.6 \times 10^{-4}$ and $15.7 \times 10^{-4} \pm 5.8 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$, respectively. Improved hole mobilities can be attributed to better charge transport within P3HT domains and through the continuous pathways induced by E-field treatment. Because of their large standard deviation (see Figure S5 and Table S4), V-films interestingly recorded minimum and maximum hole mobilities of $9.8 \times 10^{-4}$ and $21.5 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$; which are close to average hole mobility in control and H-films, respectively. Lower mobility values in V-films are due to increased edge-on conformation, in which the side chains are perpendicular to the substrate hindering the hole transport in vertical direction.\textsuperscript{49} High mobility values in V-films are due to improved crystallinity (as seen in GIWAXS results), facilitating fast charge transport along the conjugation and $\pi-\pi$ stacking directions.
Figure 4. (a) Photoluminescence (PL) spectra of P3HT:PCBM thin films (inset shows bi-exponential PL lifetimes $\tau_1$ and $\tau_2$). The PL decay was measured by the time-correlated single-photon-counting (TCSPC) method. PL spectra were collected at a probing fluorescence wavelength of 400 nm and emission wavelengths from 500 to 800 nm. The instrument response function (IRF), which is plotted in Figure 4a, has a FWHM of ca. 33 ps. (b) Dark current versus voltage characteristics of control and E-field processed P3HT:PC$_{60}$BM hole-only devices. Insets in Figure 4b show the device structure (bottom-right) and hole mobility (top-left) obtained from straight-line fitting of SCLC regime.

Combining the KPFM, GIWAXS and PL results, we construct a cartoon representation (shown in Figure 5) to demonstrate the depth profile of P3HT:PCBM BHJs. Brown arrows in Figure 5 show the direction of E-field’ lines. While the cross-section of control BHJ have large polymer aggregates (in yellow) and fullerene (in black) features (Figure 5a); H-field leads to refined nanoscale morphologies with slight increase in PCBM on the surface (Figure 5b and Figure 2f); T-field leads to large fullerene clusters on the surface and slight demixing (Figure 5c) as confirmed by KPFM maps and histograms (Figure 2c and g); and V-field hampers the intimate intermixing of P3HT/PCBM blend, leading to strong phase separation forming bilayer-like
configuration (Figure 5d). Because of morphological differences among the four BHJs, different photovoltaic behaviors of P3HT:PC_{60}BM OPVs are expected.

**Figure 5.** Cartoon representation generated by Labview based on the KPFM, GIWAXS and PL results to show the distribution of fullerenes (in black) and polymer (yellow background) in (a) control and (b-d) E-field treated P3HT:PCBM thin films. Brown arrows in (b) horizontal, (c) tilted and (d) vertical cases show the direction of the E-field’s lines.

**Figure 6a** shows the photovoltaic characteristics of conventional OPVs (structure: ITO/PEDOT:PSS/ P3HT:PCBM/ Ca/Al, inset of Figure 6a). Over eight batches, devices were highly reproducible and OPVs processed in T-field exhibit higher PCE (2.58 ± 0.02%) than the control (1.83 ± 0.10%) (see Table 1). This enhancement is attributed to an increase of ~7%, ~11% and ~18% in the open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$) and fill factor (FF), respectively. Pulling fullerene molecules toward the top metal contact with less phase separation relative to V-film, as proved by the PL data, is the reason behind the higher...
PCE of conventional OPVs processed in T-field. Conversely, OPVs exposed to H-field exhibit $J_{SC}$ ~13% lower than the control. This $J_{SC}$ decrease is ascribed to slight phase separation in P3HT:PCBM BHJ as indicated by $\tau_2$ increase (441 ps) compared to the control (378 ps) (see Figure 4a). OPVs fabricated in V-field have the poorest performance (1.06 ± 0.10%), stemming from significant decrease in $V_{OC}$ (~11%), $J_{SC}$ (~10%) and FF (~24%). This PCE decrease strongly correlates to highest P3HT:PC$_{60}$BM de-mixing and migration of the PCBM toward ITO (seen in GIWAXS, KPFM and PL lifetimes results). Other shortcomings of V-field OPVs are increased series resistance ($R_s$~249 Ω) shown in Table 1, slope (n~2.01) of $V_{OC}$ versus light intensity curve (Figure S6), and poor diode ideality factor (n~2.04), and increased saturation current in reverse bias (Figure S5). All films exposed to E-field exhibited slightly reduced optical absorbance compared the control (see Figure S7); however, the differences in thickness determined by AFM were insignificant (see Figure S9; average thickness of ~266 ± 3.6 nm). This reduced absorbance, which can be attributed to increased surface roughness as shown in AFM images (Figure S10), did not hamper solar cell performance (as in tilted OPVs). Interestingly, E-field treatment showed similar photovoltaic trend in other polymer/fullerene systems such as poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7)-based OPVs (see Figure S11).
Figure 6. Current-density versus voltage curves under AM 1.5 G illumination at one sun (100 mW/cm$^2$) of (a) conventional and (b) inverted P3HT:PC$_{60}$BM OPVs.

Table 1. Effect of E-field on the photovoltaic parameters of air-processed conventional and inverted P3HT:PC$_{60}$BM OPVs under AM 1.5 G illumination.

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<thead>
<tr>
<th></th>
<th>$V_{oc}$ (Volt)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>0.54</td>
<td>6.69 ± 0.12</td>
<td>51</td>
<td>1.83 ± 0.10</td>
<td>196</td>
</tr>
<tr>
<td>Horizontal</td>
<td>0.57</td>
<td>5.82 ± 0.29</td>
<td>57</td>
<td>1.91 ± 0.03</td>
<td>142</td>
</tr>
<tr>
<td>Tilted</td>
<td>0.58</td>
<td>7.41 ± 0.02</td>
<td>60</td>
<td>2.58 ± 0.02</td>
<td>98</td>
</tr>
<tr>
<td>Vertical</td>
<td>0.48</td>
<td>5.99 ± 0.05</td>
<td>39</td>
<td>1.06 ± 0.10</td>
<td>249</td>
</tr>
<tr>
<td>Inverted</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>0.60</td>
<td>10.48 ± 0.0</td>
<td>56</td>
<td>3.50 ± 0.0</td>
<td>161</td>
</tr>
<tr>
<td>90 s in Vertical field</td>
<td>0.61</td>
<td>11.51 ± 0.4</td>
<td>59</td>
<td>4.10 ± 0.40</td>
<td>59</td>
</tr>
<tr>
<td>30 minutes in Vertical field</td>
<td>0.54</td>
<td>5.55 ± 0.11</td>
<td>46</td>
<td>1.39 ± 0.13</td>
<td>197</td>
</tr>
</tbody>
</table>

So far, E-field treatment leads to tailored polymer/fullerene morphologies, enhanced charge transport, and improved PCE in conventional OPVs processed in T-field. However, we believe
that V-field can be utilized to achieve desirable vertical phase separation, in which more fullerenes near the cathode (top metal contact), and more polymer aggregates near the anode (ITO). We hypothesize that PCBM migration to the bottom of BHJ is a time-dependent process. In addition to control, which took ~40 minutes to dry; two substrates coated with P3HT:PCBM active layers were processed in V-field. While the first substrate was exposed to V-field for 90 seconds, the other one was left to dry in the V-field (~30 minutes). Consequently, exposing P3HT:PC_{60}BM BHJs to V-field for ninety seconds enhanced the PCE of inverted OPVs to 4.10 ± 0.4% compared to from 3.50% for the control (Figure 6b and Table 1). Ninety seconds of V-field treatment decreases the R_S of inverted OPVs from 161 Ω for the control to 59 Ω, enhancing J_SC and FF by ~9% and ~5%, respectively. 4.1% PCE efficiency is impressive considering that these inverted OPVs were fabricated in air. Inversely, inverted OPVs left to dry in V-field exhibit PCE of 1.39 ± 0.13%, which is ~60% lower than the control. 47% reduction in J_SC of inverted OPVs dried in V-field is ascribed to polymer/fullerene phase separation causing intensified radiative recombination. Comparing the FF values in inverted (FF=46%) and conventional (FF=39%) OPVs solidified in V-field, we find that PCBM segregation in inverted OPVs towards the desirable electrode (cathode) improves the FF; however, the demixing is sufficient to kill the PCE.

**Conclusions**

In conclusion, we applied a static E-field gradient to solution-processed P3HT:PCBM-based thin films and devices. We initially observe that pure droplets of organic solvent (orthodichlorobenzene) show no response to the E-field, whereas P3HT and PC_{60}BM solutions are attracted to the stronger field at the VDG surface. P3HT/PCBM thin films treated with vertical E-field exhibit reduced mosaicity and increased edge-on orientation as seen in GIWAXS results.
Phase separation is also affected in P3HT:PCBM BHJ due to differential response of polymer and fullerene to the electrostatic force of the VDG. Coarsened morphologies with large polymer and fullerene features are achieved, notably improving charge transport anisotropically dependent on the direction of E-field. Fullerenes penetrate through the “spaghetti-like” P3HT to the surface or the substrate following the E-field, leading to efficient conventional and inverted P3HT:PC<sub>60</sub>BM OPVs.

ASSOCIATED CONTENT

Supporting Information. Associated content includes Videos S1 and S2, KPFM supplementary results, Line-cuts of (100) peak in 2D-GIWAXS maps, hole-mobility results and OPVs supplementary data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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AUTHOR CONTRIBUTIONS

M.E. designed the experiments, fabricated all the devices, obtained, and analyzed the data. M.E., R.G., W.L., E.G., W.W., J.S., Z.J. and D.V. collected and analyzed the GIWAXS data. U.B. and J.P. collected the PL data. M.E. and J.C. measured the SCLC hole mobility of the hole-only devices. S.V., E.N. and Q.Q. performed the KPFM imaging. All authors discussed the results in this manuscript. M.E. developed the explanation and wrote the manuscript, which was revised by all the authors. S.C. supervised this work.

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REFERENCES


