

High Performance Organic Solar Cells Processed by Blade Coating in Air from a Benign Food Additive Solution

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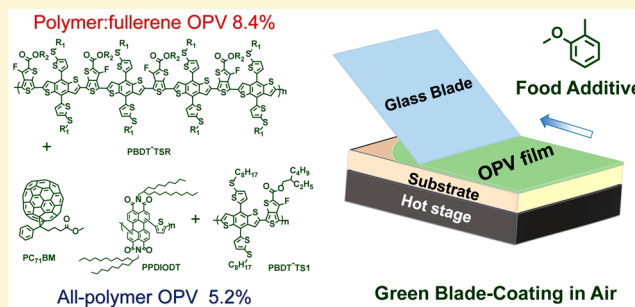
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S Supporting Information

ABSTRACT: Solution processable conjugated organic materials have gained tremendous interest motivated by their potential of low cost, lightweight and especially easy manufacturing of large-area and flexible electronics. Toxic halogen-containing solvents have been widely used in the processing of organic electronics, particularly organic photovoltaics (OPVs). To transition this technology to more commercially attractive manufacturing approaches, removing these halogenated solvents remains one of the key challenges. Our morphological (hard/soft X-ray scattering) and calorimetric characterizations reveal that using *o*-methylanisole, a certified food additive, as processing solvent can achieve similar crystalline properties and domain spacing/purity with that achieved by widely used binary halogenated solvents (chlorobenzene and 1,8-diiodooctane), thus yielding comparable photovoltaic performance in spin-casted films. To move a step forward, we further present the potential of *o*-methylanisole as processing solvent in the blade-coating of several cases of OPVs in air. Remarkably, this single nonhazardous solvent yields ~8.4% and ~5.2% efficiency in OPVs by respectively blade-coating PBDT-TSR:PC₇₁BM and all-polymeric PBDT-TS1:PPDIODT in ambient air, which are among the highest values for the respective kind of device. We postulate this simple nonhazardous solvent approach will also be applicable in the large area roll-to-roll coating and industrial scale printing of high-efficiency OPVs in air.



INTRODUCTION

Organic semiconductors based on conjugated polymers and small molecules are a large class of materials that have been extensively investigated for various applications that allow printed, flexible, stretchable, and large-area electronics like organic field-effect transistors (OFETs) and bulk-heterojunction organic photovoltaics (OPVs).^{1,2} In particular, persistent laboratory research efforts have led to OPVs with ~12% power conversion efficiency (PCE), which makes this technology an economically viable contender for commercialization.^{3,4} Such improvements have thus far been achieved only in OPV devices utilizing photoactive films formed through spin-casting from toxic halogenated solvents or binary hydrocarbon solvents in an inert environment (i.e., nitrogen-filled glovebox). Although Yan et al. achieved 11.7% PCE in spin-coated OPV devices using binary halogen-free solvents (1,2,4-trimethylbenzene and 1-phenylnaphthalene),³ these hydrocarbon solvents are still hazardous to environment and human health according to material safety data sheet. Along with the improvement in PCE, a central issue in the development of the commercial viability of

OPVs is pursuing a greener and simpler manufacturing protocol^{5,6} that allows for large-area processing in ambient air. The later demands replacing spin-casting by other printing techniques^{7–15} and using extremely low-toxicity, halogen-free solvents that do not impose any environmental or health problems.

Because the benefits of using halogenated solvent additives, such as 1,8-diiodooctane (DIO), to OPV performance was discovered,¹⁶ addition of these chemicals to various host solvents, such as chloroform (CF), chlorobenzene (CB), and dichlorobenzene (DCB), has become a widely used strategy to modulate and optimize the crystallinity, domain size, domain purity, as well as favorable surface composition in a wide range of bulk-heterojunction blends.^{3,17–24} Although great achievements have been made to optimize the morphology and device performance by selecting numerous binary combinations or

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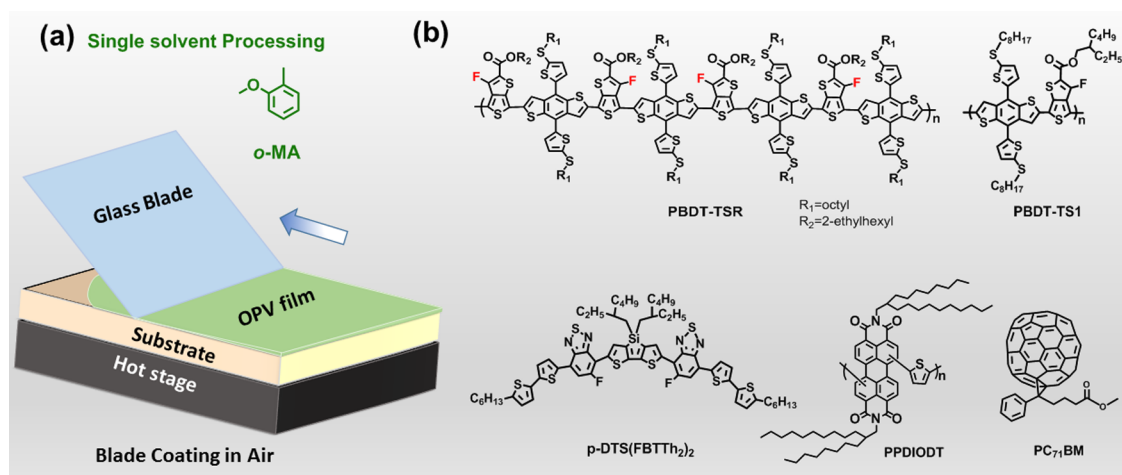


Figure 1. Schematic illustration of blade coating OPVs in air by using a single food additive *o*-MA as solvent (a) and chemical structures of the material systems (b) used in this work.

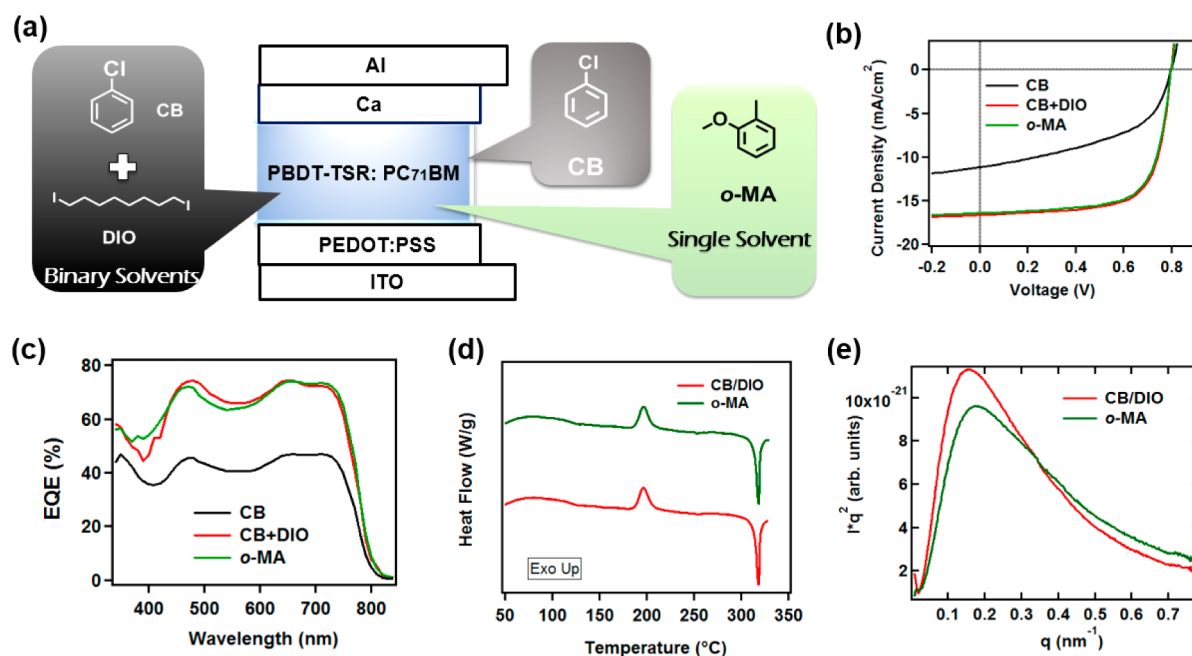


Figure 2. (a) Spin-coated OPVs based on PBDT-TSR:PC₇₁BM processed from (i) halogenated binary solvents (CB/DIO), (ii) halogenated single solvent (CB), or (iii) single green solvent (*o*-MA); (b) *J*-*V* and (c) EQE characteristics of OPVs processed from different solvents; (d) mass normalized DSC heat-only thermograms of CB/DIO and *o*-MA drop-cast films; (e) thickness normalized and Lorenz corrected R-SoXS profiles of spin-coated blends films processed from CB/DIO and *o*-MA.

ternary mixtures based on primary halogenated solvents and solvent additives, the intrinsic issues, such as toxicity, chemical degradation, morphology instability, and anomalously low reproducibility originating from high boiling-point solvent additives, will undoubtedly limit their future application.^{24,25} Furthermore, most PCE values of the state-of-the-art OPVs fabricated using nonhalogenated single solvent lag behind those processed from binary halogen-containing toxic solvents.^{26–36} Therefore, achieving high PCEs via an additive-free, single green solvent printing approach using scalable compatible printing methods is one of the great remaining challenges for commercialization of OPV technology.^{36–38}

Blade coating is a deposition technique that produces smooth and uniform thin-film and is compatible with and representative of large area, roll-to-roll printing of OPVs.^{5,7–9,13,39–41} A recent study⁹ by Richter et al. suggested

that the nanomorphology of an optimized blade-coated PffBT4T-2OD:PC₇₁BM film is considerably different from that of a spin-coated film from a ternary halogenated solvent (DCB/CB/DIO). These results challenge the current understanding that the optimization strategy is quite similar for spin-coating and blade-coating and also points out that a diverse microstructure (or morphology) likely leads to high performance printed OPV devices. To accelerate the process of developing a set of easily printable materials for OPV, particularly those processed with single green solvent, a complete characterization of their complex and hierarchical morphology is highly desired.

With the exception of a few reports,^{14,15,41} little attention has been given to using a single green solvent to blade-coat OPV devices in air. This is particularly true for high performance material systems, where the PCE reported in the previous

Table 1. Device Parameters of Spin-Coated PBDT-TSR:PC₇₁BM OPVs with Various Cast Solvents under AM1.5G 100 mA/cm²

cast solvent	thickness [nm]	V _{oc} [mV]	J _{sc} [mA/cm ²]	FF [%]	PCE ^a [%]
CB	100	802 ± 5	11.49 ± 0.37	48.60 ± 1.96	4.47 ± 0.14 (4.73)
CB/DIO	100	788 ± 4	17.36 ± 0.27	66.19 ± 1.79	9.06 ± 0.31 (9.60)
<i>o</i> -MA	95	789 ± 3	17.61 ± 0.27	67.63 ± 1.31	9.40 ± 0.19 (9.65)

^aThe values in the parentheses are from the best devices and the statistics are from 20 devices.

studies were limited to less than 4%. In this contribution, we demonstrate for the first time PCEs surpassing 8% and 5% in blade coated fullerene-based and all-polymeric OPV devices, respectively, fabricated in air using a single green solvent. The films were comprised of a recently developed low bandgap polymer PBDT-TSR⁴² as a prototype system, along with some additional material systems, which were dissolved in the environmentally benign solvent *o*-metylanisole (*o*-MA, chemical structure shown in Figure 1), a known food ingredient (see details in Supporting Information). Although some anisole derivatives have been used in spin-coated OPV devices,^{36–38} the utility of this class of solvents in printed devices have not yet been studied. Moreover, the hierarchical structure in the promising air-processed OPV devices cast from the food additive solution are quantified and discussed based on analysis of transmission resonant soft X-ray scattering (R-SoXS) coupled with atomic force microscopy (AFM). This study therefore, highlights the great opportunity of single food additive solutions to realize high performance OPV devices using a scalable processing method in an ideal manufacturing environment (i.e., air).

RESULTS AND DISCUSSION

Halogenated solvents are used because they dissolve most organic semiconductors well. However, as OPVs technology approaches commercialization, the need for cost-effective and safe processing protocols is becoming more pertinent. Here, we used the polymer PBDT-TSR, a PTB7-analogue polymer with regioregular structure, which shows promising photovoltaic properties including narrow optical bandgap (~1.5 eV), high hole mobility of $3.16 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, enhanced solid-state packing order, and high absorption coefficient over 10^5 cm^{-1} , altogether giving rise to high PCE over 9% for solid films processed from binary chlorobenzene (CB)/1,8-diodooctane (DIO) at relatively low temperature (<100 °C) and thin film with thickness around 100 nm.⁴² Additionally, a low-lying HOMO level of −5.35 eV may enable PBDT-TSR stability in air. Inspired by a recent study,³⁸ we now find this polymer also dissolves well in the target *o*-MA solvent due to the long alkyl chains. *o*-MA has a moderate boiling point and solubility, thereby allowing the spin-coating of two commercially available material systems with good performance under nitrogen-filled inert atmosphere.

To check the utility of *o*-MA in OPV fabrication of PBDT-TSR, we first investigated the photovoltaic performances of spin-coated PBDT-TSR:PC₇₁BM blend with a conventional OPV device configuration (Figure 2a) by comparing *o*-MA with two common halogenated solvent systems (CB, CB/DIO) in inert atmosphere. The photovoltaic parameters tested under simulated 100 mW cm^{−2} AM 1.5G illumination are summarized in Table 1 and Figure 2b,c. Statistical results based on 20 devices indicate that both CB/DIO and *o*-MA processed OPVs show approximately 2-fold increase in PCE compared to devices processed from CB due to the increases of both short-circuit current density (*J*_{sc}) and fill factor (FF). The PCEs of

the spin-coated OPVs processed with *o*-MA give an average value of 9.40% with a small standard deviation. Clearly, higher PCE along with excellent reproducibility can be easily achieved in *o*-MA processed OPVs, compared with OPVs processed with CB/DIO.

To further elucidate the underlying effect of the solvent during the process of film formation, differential scanning calorimetry (DSC) was used to examine the microstructure and crystalline features of blend films drop-cast from *o*-MA and CB/DIO. The DSC heat-only traces are shown in Figure 2d and are normalized to the mass of the sample. As PBDT-TSR is a low crystalline polymer without any melting/crystallization transition as shown in the DSC trace (Figure S1), the changes in the PC₇₁BM feature reflect the microstructure information of blend films. The melting (~310 °C) and crystallization (~200 °C) transitions area and peak positions of PC₇₁BM are almost identical for both blend films processed from *o*-MA and CB/DIO. This observation is consistent with two-dimensional grazing incidence X-ray diffraction (GIXRD) characterization of spin-cast films (Figure S2). Accordingly, there is a similar microstructure between films spin-cast from CB/DIO and *o*-MA.

Quantitative nanomorphology characterizations of the films processed from *o*-MA and CB/DIO were further carried out with transmission R-SoXS, and two key morphological metrics, domain length scale and average domain purity, of the blend films were derived.^{18,19} A resonant photon energy of 284.2 eV is selected to maximize the material contrast, as shown in Figure S3, which is derived from the near-edge X-ray absorption fine structure spectroscopy (NEXAFS) spectra of neat PBDT-TSR and PC₇₁BM films. The intensities of the R-SoXS profiles (Figure 2e) were corrected for absorption following the Beer–Lambert law and normalized by thickness to account for the number of scattering centers.⁴³ Both of the films processed by *o*-MA and CB/DIO show a dominant peak located at the same position around $q = 0.16 \text{ Å}^{-1}$, corresponding to a long period (domain spacing) of ~40 nm. Multipeak fit of the R-SoXS profiles also show a similar result (Figure S4). The similar domain lengths observed in *o*-MA and CB/DIO processed films support the comparable *J*_{sc} results and EQE values (Figure 2c).⁴³ By integrating the R-SoXS profiles and ensuring that scattering originates from optical contrast between polymer-rich and fullerene-rich domains, the integrated scattering intensity (ISI) reflects the relative composition variations (i.e., average purity over all domains) between the blends over the length scales probed. Compared with CB/DIO, *o*-MA yields a slightly higher ISI and thus corresponds to purer domains, which is consistent with the trend of device FFs.^{3,43} Combining the photovoltaic and morphological results, *o*-MA can potentially replace binary halogenated solvents (CB/DIO), and greatly outperform a single halogenated solvent (CB) in fabricating high-efficiency OPVs.

After demonstrating the use of *o*-MA with spin-coating, we turn our attention to blade coating in air, which is a roll-to-roll compatible large-area coating technique with minimal material

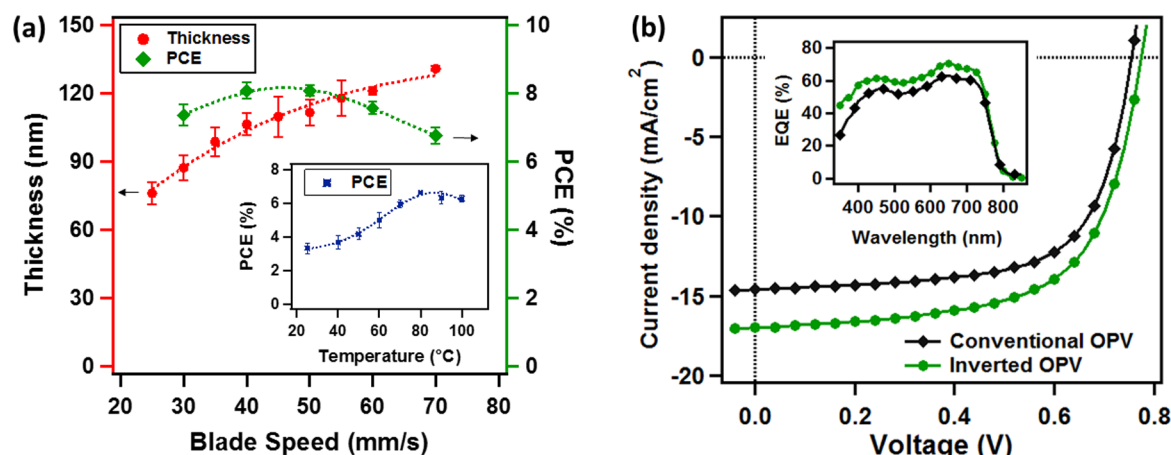


Figure 3. (a) PCEs of OPVs from blade-coated PBDT-TSR:PC₇₁BM blend films as a function of temperature, and thickness and PCEs of OPVs from blade-coated PBDT-TSR:PC₇₁BM blend films as a function of blade speed; (b) *J*-*V* and EQE curves of best-performing *o*-MA blade-coated PBDT-TSR:PC₇₁BM devices in conventional and inverted device geometries.

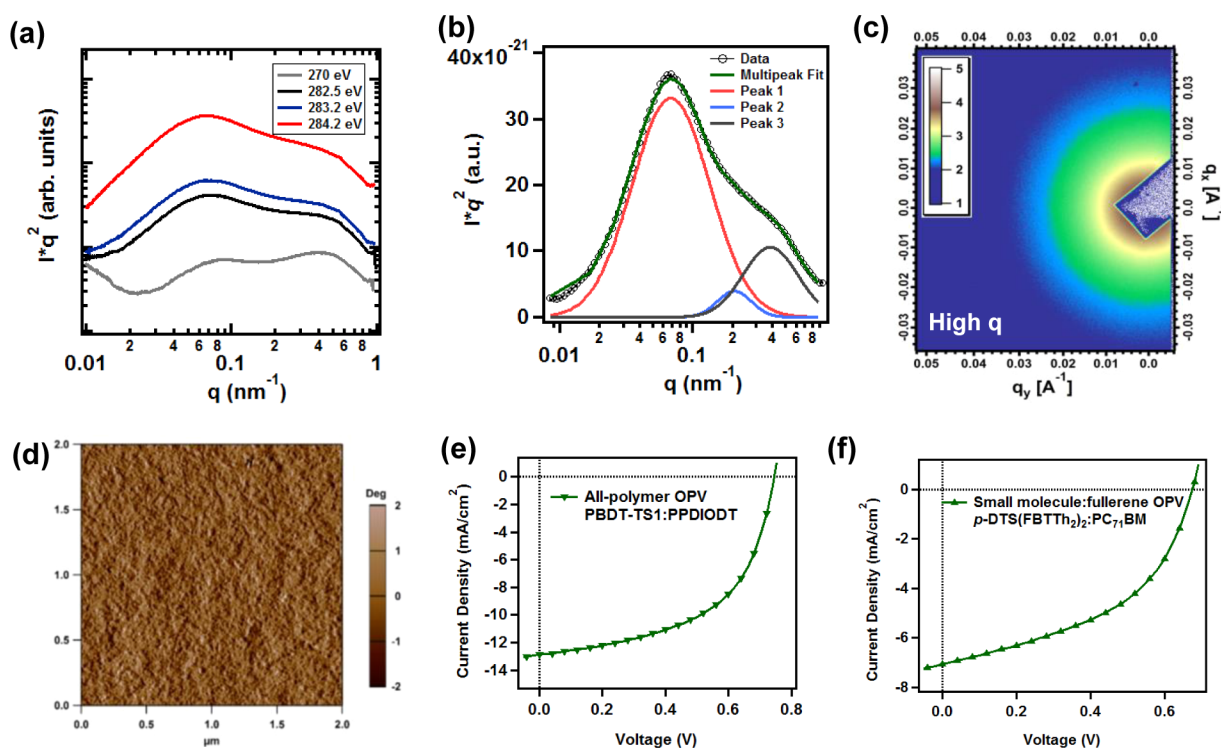


Figure 4. (a) 1D circularly averaged R-SoXS profiles of green solvent blade-coated PBDT-TSR:PC₇₁BM film acquired at various energies; (b) 1D circularly averaged R-SoXS profile multipole fitting using three log-normal peaks and (c) 2D R-SoXS pattern of green solvent blade-coated PBDT-TSR:PC₇₁BM film acquired at 284.2 eV; (d) AFM phase image of PBDT-TSR:PC₇₁BM blend film by blade coating with *o*-MA in air; *J*-*V* curves of blend films based on PBDT-TS1:PPDIODT (e) and *p*-DTS(FBTTh₂)₂:PC₇₁BM (f) by blade coating with *o*-MA in air.

waste.^{5,9} A custom blade coater is employed similar to one previously described in detail,⁴⁴ with a schematic of the process presented in Figure 1a. The performance of inverted OPVs comprising PBDT-TSR:PC₇₁BM photoactive blend was optimized by varying the temperature of the hot stage and the blade speed (Figure 3a). From a set of control experiments, the optimal processing temperature was found to be 80 °C (Figure 3a), which is in sharp contrast with the room-temperature spin-coating condition.⁴² The blade speed is known to be a critical parameter affecting OPV device performance. For the investigated coating speed window (20–80 mm/s), the thickness of the PBDT-TSR:PC₇₁BM film increases with the blade speed and thus the Landau–Levitch regime⁴⁵ dominates

the film deposition in this case. In Figure 3a, we have plotted the PCE as a function of blade speed (thickness) and the device PCEs are above 7% for film thickness ranging from 70 to 120 nm. The inverted OPV device prepared at optimal conditions (80 °C; ~100 nm) exhibits an average *J*_{sc} of over 16 mA/cm², a FF of ~62%, and an open-circuit voltage of ~0.78 V, resulting in an average PCE up to 8.0% under AM1.5G 100 mW/cm² irradiation. The external quantum efficiency (EQE) characteristic shows a broad optical response range with a peak value close to 70%.

The best-performing inverted device exhibited a maximum PCE of 8.38%, which significantly outperforms blade-coated devices in many earlier reports. For comparison, Tables S1

Table 2. Device Parameters of Various OPVs from Blade-Coating with *o*-MA in Air

blend system	V_{oc} [mV]	J_{sc} [mA/cm ²]	FF [%]	PCE ^c [%]
PBDT-TSR:PC ₇₁ BM ^a	759 ± 8	13.95 ± 0.41	66.25 ± 1.48	7.01 ± 0.15 (7.38)
PBDT-TSR:PC ₇₁ BM ^b	780 ± 5	16.48 ± 0.27	62.37 ± 0.39	8.02 ± 0.12 (8.36)
PBDT-TS1:PPDIODT ^b	744 ± 3	12.79 ± 0.74	53.42 ± 1.85	5.07 ± 0.12 (5.21)
<i>p</i> -DTS(FBTTh ₂) ₂ :PC ₇₁ BM ^b	688 ± 9	6.27 ± 0.56	42.44 ± 2.82	1.84 ± 0.27 (2.22)

^aConventional device configuration of ITO/PEDOT:PSS/blend/Ca/Al. ^bInverted device configuration of ITO/ZnO/blend/MoO₃/Al; ^cThe values in the parentheses are from the best devices and the statistics are from 20 devices.

provides a list of reported blade-coated OPV devices and associated device performance data. To the best of our knowledge, the PCE of 8.4% reported herein is the highest achieved for OPV devices blade-coated in air using any reported halogen-free solvent systems. To evaluate the effect of device configuration on solar cell performance, we found the inverted PBDT-TSR:PC₇₁BM OPV devices outperforms conventional OPV devices, which show an average PCE of 7.01% under optimal conditions (Figure 3b).

Understanding of the complex morphology remains largely unexplored for the blade-coated OPV films from halogen-free solvents. Here, the R-SoXS profiles (Figure 4a) for the optimized blade-coated PBDT-TSR:PC₇₁BM film show distinct multiple-length scale structural features and phase separations at various q values at various soft X-ray energies. This hierarchical or multilength scale phase separation feature has been observed in several OPV systems,^{46–52} including PTB7:PC₇₁BM, PDPP3T:PC₇₁BM, PBDTTPD:PC₆₁BM. Hierarchical structures lead to improved efficiencies in spin-coated devices by establishing efficient exciton dissociation and charge collection processes. The scattering at energies near the absorption edge (~284 eV) of both materials are dominated by the material contrasts. Three peaks, which are located at $q = 0.07, 0.21, \text{ and } 0.38 \text{ nm}^{-1}$, corresponding to the characteristic length scales of 89.8, 29.9, and 16.5 nm, respectively, are clearly shown in the scattering profile acquired at high material contrast (284.2 eV) (Figure 4b,c). The presence of reasonably small domain length of 16.5 nm enables efficient charge creation and minimizes the charge recombination, as is well-illustrated in a recent study.⁴⁶ The two smaller peaks are roughly consistent with those measured for the spin-coated film (Figure S4), whereas the largest length scale at low- q around 0.07 nm^{-1} represents larger aggregate features, as evidenced by the AFM height image of PBDT-TSR:PC₇₁BM blend film (Figure S5). The power spectral density (PSD)⁴⁹ analysis of AFM phase image (Figure 4d) as depicted in Figure S6 shows strong correlations with the distinct scattering peaks derived from R-SoXS, again verifying the existence of multilength morphology. It is also noteworthy that the R-SoXS profile of our blade-coated PBDT-TSR:PC₇₁BM device is more complex than that of spin-coated device, which is consistent with the observation in the PffBT4T-2OD:PC₇₁BM system as shown by Richter et al.⁹ These observations suggest hierarchical morphology may be a common feature of printed OPVs, regardless of the solvent types and material systems used.

To further explore the feasibility of our single, benign solvent approach for other promising material systems, a high-efficiency all-polymeric blend PBDT-TS1:PPDIODT³⁷ and a benchmark small molecule:fullerene blend *p*-DTS(FBTTh₂)₂:PC₇₁BM,⁵³ were tested using air processing (Figure 4e,f). As shown in Table 2, blade coating using *o*-MA solvent works well in both material systems. Strikingly, a high PCE up to 5.2% is also achieved in blade-coated all-polymer OPV, which is also a

record efficiency for all-polymer OPVs by blade coating in air, irrespective of solvent used, and outperform the most recent blade fabricated all-polymer OPV device reported by Bao et al.⁵⁴ This indicates that blade-coating from a single, nontoxic solvent will be applicable in creating environmentally friendly inks for air processing nonfullerene OPVs. From the case study of blade-coated PBDT-TSR:PC₇₁BM, measurement of crystallization/melting features of blend films by DSC and GIXRD may allow identification of more green solvent candidates, which can produce comparable or outperform results achieved from halogenated solvents.

CONCLUSIONS

The nanomorphology and microstructure observations based on R-SoXS, DSC, and GIWAXS indicate *o*-MA, an extremely low toxicity solvent and certified food additive, yields similar crystalline features, similar morphology (i.e., domain spacing and composition), and thus comparable device performance with those achieved by a widely used binary halogenated solvents (CB/DIO) in spin-coated OPV film. After shifting to blade-coating, we are able to realize high performance, additive-free OPVs processed from *o*-MA solution in air. Remarkably, an impressive efficiency of ~8.4% and good reproducibility were achieved in OPV devices featuring a regioregular polymer PBDT-TSR, blade coated in air from this single green solvent. Our study provides the very first demonstration of over 8%-efficiency, blade-coated OPV in air with a single, truly green and benign solvent. The *o*-MA blade coated PBDT-TSR:PC₇₁BM film shows a multilength scale morphology as revealed by R-SoXS and AFM. Additional tests of two representative material systems including small molecular *p*-DTS(FBTTh₂)₂:PC₇₁BM, and fullerene-free all-polymer PBDT-TS1:PPDIODT further demonstrate the great potential of *o*-MA processing. From manufacturing standpoint, *o*-MA is an environmentally friendly solvent to process several representative organic photovoltaic materials in air with high efficiency and thereby significantly decreasing the risk to human health and reducing the cost for large scale production of OPV. Our eco-friendly approach will be very beneficial to manufacture OPVs with efficiency over 10% while the ability to process devices in ambient conditions drastically reduces manufacturing cost. We expect higher performance can be achieved in a wide range of material systems by further optimizing the food additive solution processing, which will also be applicable in fabricating other kinds of thin-film organic electronics such as transistors or light-emitting diodes.

EXPERIMENTAL SECTION

Materials. PBDT-TSR ($M_n = 30 \text{ kDa}$; PDI = 2.1), PBDT-TS1 ($M_n = 29 \text{ kDa}$; PDI = 2.2), and PPDIODT ($M_n = 13.6 \text{ kDa}$; PDI = 1.38) were synthesized in the Hou lab. *p*-DTS(FBTTh₂)₂ was sourced from One-Materials Inc. PC₇₁BM (purity > 99%) was purchased from American Dye Inc. *o*-MA, CB, and DIO were provided by Sigma-

Aldrich. All materials were used as received without further purification.

Methods. OPV devices were fabricated with a structure of glass/ITO/PEDOT:PSS/active layer/Ca/Al or glass/ITO/ZnO/active layer/MoO₃/Al. PEDOT:PSS (4083) was spin-coated at 4000 rpm onto ITO substrate, followed by annealing at 150 °C for 15 min. For the inverted devices, a thin layer of ZnO (~30 nm) was spin-coated onto precleaned ITO-coated glass substrates and then annealed at 180 °C for 1 h in air. The active layer was spin-coated from a homogeneous solution of PBDT-TSR (8 mg/mL) and PC₇₁BM (12 mg/mL) onto the PEDOT:PSS layer. CB, CB/3%DIO, and *o*-MA were respectively used as processing solvent. Finally, 30 nm calcium/90 nm aluminum were thermally evaporated as cathodes under vacuum (8×10^{-7} Torr). The active area of each device is 6.9 mm². For blade-coated samples, the D/A ratio and total concentration are the same with that used in spin-coated devices.

Instruments. All blade-coating experiments were performed using a custom built system, and the detailed setup of our blade-coater is provided in the [Supporting Information](#). The *J*–*V* characteristics were measured with a Keithley 2400 source meter under illumination of an AM1.5G solar simulator (Oriel Sol3A, Newport Corporation) with an intensity of 100 mW/cm². *J*–*V* and EQE measurements were conducted in a glovebox. Samples cast from different solvents were performed on a TA Instruments Discovery DSC using a heat–cool–heat procedure and a heating/cooling rate of 10 °C/min. Resonant soft X-ray scattering (R-SoXS)⁵⁵ was performed in transmission geometry with linearly polarized photons under high vacuum (1×10^{-7} Torr) at beamline 11.0.1.2 at the Advanced Light Source (ALS), and the scattering patterns were recorded by a Princeton PI-MTE CCD detector (2048 pixels $\times$ 2048 pixels). The soft X-ray energy was tuned between 270 and 290 eV in the R-SoXS experiments. The two-dimensional images were processed using a modified form of the Nika software package⁵⁶ implemented within Igor. The NEXAFS and GIWAXS experiments were respectively done under Helium atmosphere at beamline 5.3.2.2⁵⁷ and 7.3.3⁵⁸ at the ALS. Film thickness was measured with a KLA-Tencor P-15 profilometer.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/acs.chemmater.6b03083](#).

Detailed properties of solvents, NEXAFS contrast functions, experimental setup of blade-coater, and detailed analysis of DSC, GIWAXS, AFM, and R-SoXS (PDF)

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Notes

The authors declare no competing financial interest.

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