

Achieving Efficient Thick Film All-polymer Solar Cells Using a Green Solvent Additive

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Electronic Supplementary Information

Abstract Advances in organic photovoltaic technologies have been geared toward industrial high-throughput printing manufacturing, which requires insensitivity of photovoltaic performance regarding to the light-harvesting layer thickness. However, the thickness of light-harvesting layer for all polymer solar cells (all-PSCs) is often limited to about 100 nm due to the dramatically decreased fill factor upon increasing film thickness, which hampers the light harvesting capability to increase the power conversion efficiency, and is unfavorable for fabricating large-area devices. Here we demonstrate that by tuning the bulk heterojunction morphology using a non-halogenated solvent, cyclopentyl methyl ether, in the presence of a green solvent additive of dibenzyl ether, the power conversion efficiency of all-PSCs with photoactive layer thicknesses of over 500 nm reached an impressively high value of 9%. The generic applicability of this green solvent additive to boost the power conversion efficiency of thick-film devices is also validated in various bulk heterojunction active layer systems, thus representing a promising approach for the fabrication of all-PSCs toward industrial production, as well as further commercialization.

Keywords Thick-film all-polymer solar cell; Green solvent additive; Dibenzyl ether

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INTRODUCTION

Polymer solar cells (PSCs) are continually considered as an interesting lightweight, low-cost, and short-energy-payback-time technology for future roll-to-roll industrial mass production by printing flexibly large area photovoltaic modules.^[1–8] Particularly, all-polymer solar cells (all-PSCs), which comprise of p-type polymeric semiconductors as electron donors and n-type conjugated polymers as electron acceptors in the light-harvesting layer, have attracted growing interests on account of the excellent mechanical and environmental stability.^[9–13] Through rational molecular design of the light-harvesting materials and meticulous manufacturing of the light-harvesting bulk heterojunction (BHJ) layers of all-PSCs, the realized power conversion efficiencies (PCEs) have been prominently boosted from below 4% to about 11% in recent years, demonstrating great potential toward practical applications.^[14–23]

One of the most intricating issues limiting the photovolt-

aic property of all-PSCs is the oversensitivity of PCE to the film thickness of the light-harvesting layer, which can be attributable to the inferior bulk charge mobility caused by anisotropic charge transport in polymeric acceptors.^[24] Although increasing the film thickness of the light-harvesting layer can lead to higher short-circuit current density (J_{sc}) and thus improved PCEs,^[25–28] the optimal thickness of the light-harvesting layer in all-PSCs is typically around 100 nm.^[29] This is due to the fact that increasing film thickness will lead to the dramatically decreased fill factor (FF), which can be correlated to the increased bimolecular recombination of charge carrier and the generation of space charge in the photoactive layer.^[30–33] One effective solution to address these issues is to increase the charge transport in the photoactive layer via rational material design.^[34–38] However, the cost and payoff of these strategies remain dubious because no rational molecular design principle has yet been established to achieve high charge transport ability. An alternative strategy is to boost charge carrier mobility by controlling the aggregation behavior of the polymer chains and BHJ film morphology.^[39,40]

Considering that the incorporation of solvent additives into the processing solvent can promote the achievement of ideal phase separation and regular molecular orientation

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of BHJ film morphology, it is of vital importance to select effective solvent additives with eligible boiling points and appropriate volatility.^[41] At the current stage, the most widely selected solvent additives for morphology optimization are 1-chloronaphthalene (1-CN) and 1,8-diiodooctane (DIO).^[42–45] The critical issue of the chlorinated 1-CN and DIO during the fabrication of PSCs is their toxicity, which is detrimental to environment and human beings toward mass-production. To address this issue, we have systematically gone through the data bank of common solvents and chosen a non-chlorinated hydrophobic ether solvent additive, dibenzyl ether (DBE, with a boiling point of 298 °C), which can potentially replace the extensively used hazardous halogenated solvent additives to not only realize sustainability but also decrease the operational costs and environmental impact.^[46] Remarkably, the all-PSCs processed with DBE as the solvent additive, which consist of a wide-bandgap p-type polymeric semiconductor PTzBI-Si and an n-type conjugated polymer N2200 (with molecular structures shown in Fig. 1a),^[47] presented an impressive PCE of 9.0% at a thickness of 520 nm, which obviously outperform those processed without DBE. More importantly, we also realized that DBE can be used as a universal green solvent additive to process a series of light-harvesting layers of thick-film PSCs to achieve improved photovoltaic performances.

EXPERIMENTAL

Materials

PTzBI-Si and N2200 were synthesised according to procedures reported in literature.^[47,48] CPME and DBE were purchased from Sigma-Aldrich without further purification.

Fabrication of Polymer Solar Cells

Indium tin oxide (ITO)-coated glass substrates were successively cleaned by sonication in detergent, deionised water, acetone, and isopropyl alcohol and dried in an oven at 75 °C for 6 h prior to use. The substrates were then exposed to oxygen plasma for 1 min and spin-coated with PEDOT:PSS (Clevios P VP Al 4083) at 3000 r·min⁻¹ for 30 s. The coated substrates were annealed at 150 °C on a hot plate for 20 min in air to produce 40-nm thin films. After annealing, they were transferred to a glove box under N₂ atmosphere. The total concentration of PTzBI-Si and N2200 was fixed at 11 mg·mL⁻¹, and the blend films were obtained by spin-coating solutions of the polymers in CPME containing different contents of DBE (vol%); to obtain active layer of PTzBI-Si:N2200 with higher thicknesses of 210, 370, and 520 nm, we kept a higher constant total concentration of PTzBI-Si and N2200 of 11 mg·mL⁻¹ and employed varied rotating speed of 3000, 900, and 450 r·min⁻¹, respectively. The photoactive layers were then thermally annealed at 110 °C for 10 min, followed by spin-coating of a 5-nm layer of PFNDI-Br at

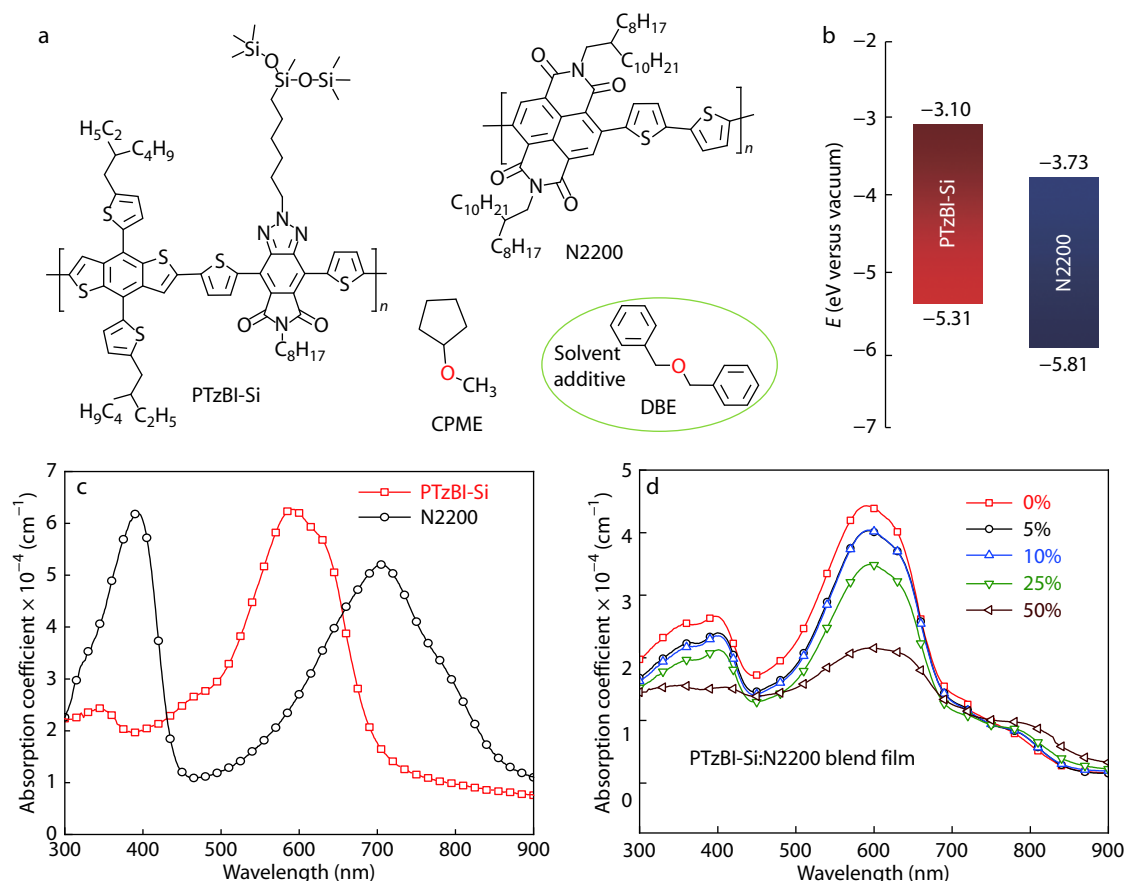


Fig. 1 (a) Molecular structures of PTzBI-Si, N2200, CPME, and solvent additive DBE; (b) Energy-level alignments of neat PTzBI-Si and N2200 films; (c) UV-Vis-NIR absorption spectra of neat PTzBI-Si and 500-nm-thick N2200 films; (d) UV-Vis-NIR absorption spectra of 500-nm-thick PTzBI-Si:N2200 blended films processed using CPME with different DBE contents.

2000 r·min⁻¹ for 30 s to serve as the cathode interface. A 100-nm argentum (Ag) layer was then thermally deposited onto the active layer through a shadow mask in a vacuum chamber with a base pressure of 2×10^{-4} Pa. The effective area of the devices (0.04 cm²) was determined by the shadow mask.

Fabrication and Characterisation of Charge-only Devices

The hole mobility was measured in a hole-only device with the configuration of ITO/PEDOT:PSS/active layer/Ag. The electron mobility was measured in an electron-only device with the configuration of ITO/ZnO/active layer/PFNDI-Br/Ag. The ZnO sol-gel was obtained from stirring the solution of 1.0 g Zn(CH₃COO)₂·2H₂O in 10 mL ethylene glycol monomethyl ether and 275 μ L ethylenediamine at 60 °C for 12 h. The total concentration of PTzBI-Si and N2200 was fixed at 11 mg·mL⁻¹, and the blend films were obtained by spin-coating solutions of the polymers in CPME containing different contents of DBE (vol%); to obtain active layer of PTzBI-Si:N2200 with higher thicknesses of 210, 370, and 520 nm, we kept a higher constant total concentration of PTzBI-Si and N2200 of 11 mg·mL⁻¹ and employed varied rotating speed of 3000, 900, and 450 r·min⁻¹, respectively. The mobility (μ) was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by Eq. (1)

$$J = (9/8) \epsilon_0 \epsilon_r \mu V_{\text{eff}}^2 / d^3 \quad (1)$$

where J is the current density, μ is the charge (hole or electron) mobility at zero field, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layer, and V_{eff} is the effective voltage ($V - V_{\text{bi}}$). The charge (hole or electron) mobility was calculated from the y intercept of the J - V curves.

Instruments and Characterisation

The absorption spectra of the film and solution samples were measured using a UV-Vis spectrophotometer (HP 8453, photodiode array type) in the wavelength range of 300–1000 nm. PL spectra were recorded on a Jobin-Yvon FluoroMax-4 spectrofluorometer. The current density-voltage (J - V) characteristics were measured using a computer-controlled Keithley 2400 SourceMeter under 1 sun irradiation from an AM 1.5 G solar simulator (Taiwan, Enlitech, SS-F5). Tapping-mode AFM images were obtained by using a Bruker multimode microscope.

Grazing Incidence Wide-angle X-ray Scattering (GIWAXS)

GIWAXS characterization of the thin films was performed at beamline 7.3.3 of Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL). The X-ray beam energy was 10 keV. The sample to detector distance was ~280 mm calibrated with AgB and the incidence angle was 0.16° normalized by a photodiode. All the GIWAXS signals were recorded in helium atmosphere with exposure time of 5 s per image using a 2D charge-coupled device (CCD) detector (Pilatus 2M) with a pixel size of 0.172 mm by 0.172 mm. Thin film samples were spin-coated on PEDOT:PSS/silicon wafer substrates.

Resonant Soft X-ray Scattering (R-SoXS)

RSoXS was performed at beamline 11.0.1.2 of Advanced Light Source, LBNL. Sample preparation was the same as that of GIWAXS samples. The thin films were floated in deionized water

and transferred on silicon nitride (Si₃N₄) windows, and subsequently the samples were loaded onto a holder. After the films were dried in air, the holder was transferred into the vacuum chamber for RSoXS. The beam energy was screened from 280 eV to 290 eV, with a 10 s exposure time per energy. The scattering patterns were collected in vacuum using a Princeton Instrument PI-MTE CCD camera with a pixel size of 0.027 mm by 0.027 mm. RSoXS data of each sample were recorded at two sample-to-CCD distance of 50 and 150 mm.

RESULTS AND DISCUSSION

The lowest unoccupied molecular orbital (LUMO) energy difference and the highest occupied molecular orbital (HOMO) energy difference between PTzBI-Si and N2200 were greater than the 0.3–0.5 eV binding energy of photon-generated excitons, resulting in effective exciton dissociation and fast charge transfer (Fig. 1b). The strong absorption band of neat PTzBI-Si covered the spectrum at 450–650 nm, which was coincidentally complementary with the range of neat N2200 that had two disparate strong absorption bands in the range of 300–450 and 650–800 nm (Fig. 1c). The absorption spectra of 500-nm-thick PTzBI-Si:N2200 blended films processed using cyclopentyl methyl ether (CPME) with 0%–10% DBE exhibited high absorption coefficients (Fig. 1d), which is desirable for efficient light harvesting and leads to J_{SC} in the all-PSCs.

The photovoltaic performance of PTzBI-Si:N2200-based all-PSCs processed with CPME containing DBE was evaluated based on a conventional structure: ITO/PEDOT:PSS/PTzBI-Si:N2200/PNDIT-F3N-Br/Ag. Here, 5-nm-thick PNDIT-F3N-Br cathode layer was deposited onto the top of the pre-deposited PTzBI-Si:N2200 layer to achieve efficient charge extraction.^[49] To investigate the role of DBE in fabricating efficient thick-film all-PSCs, we varied the active layer thickness from 210 nm to 520 nm. The open-circuit voltage (V_{OC}), J_{SC} , FF, and PCE for all-PSCs based on PTzBI-Si:N2200 films with different thicknesses that were processed with CPME in the presence of various volume ratios of DBE are summarized in Table 1.

The devices processed using CPME containing different ratios of DBE are referred to as 0%–50% DBE devices. For the 0% DBE devices (processed using CPME without DBE), the 210 nm PTzBI-Si:N2200 layer device exhibited a PCE of 9.3%. However, PCE values gradually decreased with the increased PTzBI-Si:N2200 layer thickness owing to the dramatically dropped FF (Fig. 2), where a moderate PCE of about 5% was achieved at a PTzBI-Si:N2200 layer thickness of 520 nm. The incorporation of 5% DBE as the solvent additive led to less pronounced reduction in PCE, which slightly reduced from 8.9% to 7.9% with the PTzBI-Si:N2200 layer thickness enhanced from 210 nm to 520 nm. Interestingly, the all-PSCs processed with 10% DBE presented insensitivity PCE to the thickness variation of PTzBI-Si:N2200 layer, for which the PCE achieved 8.4%, 8.5%, and 9.0% at the PTzBI-Si:N2200 layer thickness of 210, 370, and 520 nm, respectively. To our knowledge, the PCE value of 9.0% is the highest value yet reported for single-junction all-PSCs with an active layer thickness of over 500 nm,^[23,50] which demonstrates the great potential of using DBE as a solvent additive for processing thick-film all-PSCs. Further increasing the DBE content to 25% and 50% led to dramatically decreased PCEs of all-PSCs owing to the signi-

Table 1 Device parameters of all-PSCs based on PTzBI-Si:N2200 films that were processed with CPME in the presence of various volume ratios of DBE.

Solvent additive ^a	Thickness (nm)	V_{OC} (V)	J_{SC} ^b ($\text{mA}\cdot\text{cm}^{-2}$)	FF (%)	PCE _{avg} ^c (%)	PCE _{max} (%)
0% DBE	210	0.87	14.6 ± 0.2	72.7 ± 0.5	9.1 ± 0.2	9.3
	370	0.86	16.1 ± 0.3	46.4 ± 0.8	6.4 ± 0.2	6.6
	520	0.84	16.7 ± 0.8	38.1 ± 0.8	5.2 ± 0.1	5.3
5% DBE	210	0.85	13.3 ± 0.3	78.2 ± 0.5	8.8 ± 0.1	8.9
	370	0.83	14.5 ± 0.4	69.9 ± 1.1	8.3 ± 0.1	8.4
	520	0.83	16.5 ± 0.5	58.0 ± 0.8	7.7 ± 0.2	7.9
10% DBE	210	0.85	12.6 ± 0.6	79.1 ± 0.9	8.2 ± 0.2	8.4
	370	0.84	14.2 ± 0.8	72.1 ± 0.8	8.4 ± 0.1	8.5
	520	0.84	16.4 ± 0.5	63.2 ± 0.8	8.7 ± 0.3	9.0
25% DBE	210	0.85	11.9 ± 0.7	75.9 ± 0.6	7.5 ± 0.2	7.7
	370	0.84	13.6 ± 0.4	68.8 ± 0.9	7.8 ± 0.1	7.9
	520	0.84	14.7 ± 0.8	61.4 ± 0.8	7.4 ± 0.2	7.6
50% DBE	210	0.84	7.6 ± 0.5	37.2 ± 0.5	2.3 ± 0.1	2.4
	370	0.83	6.1 ± 0.7	38.4 ± 0.8	1.9 ± 0.2	2.1
	520	0.83	8.4 ± 0.3	39.7 ± 0.7	2.7 ± 0.1	2.8

^a The weight ratio of PTzBI-Si:N2200 was 2:1 and the blend film was treated with 110 °C for 10 min; ^b Obtained from J - V curves; ^c PCE values in parentheses were obtained from 15 separate devices.

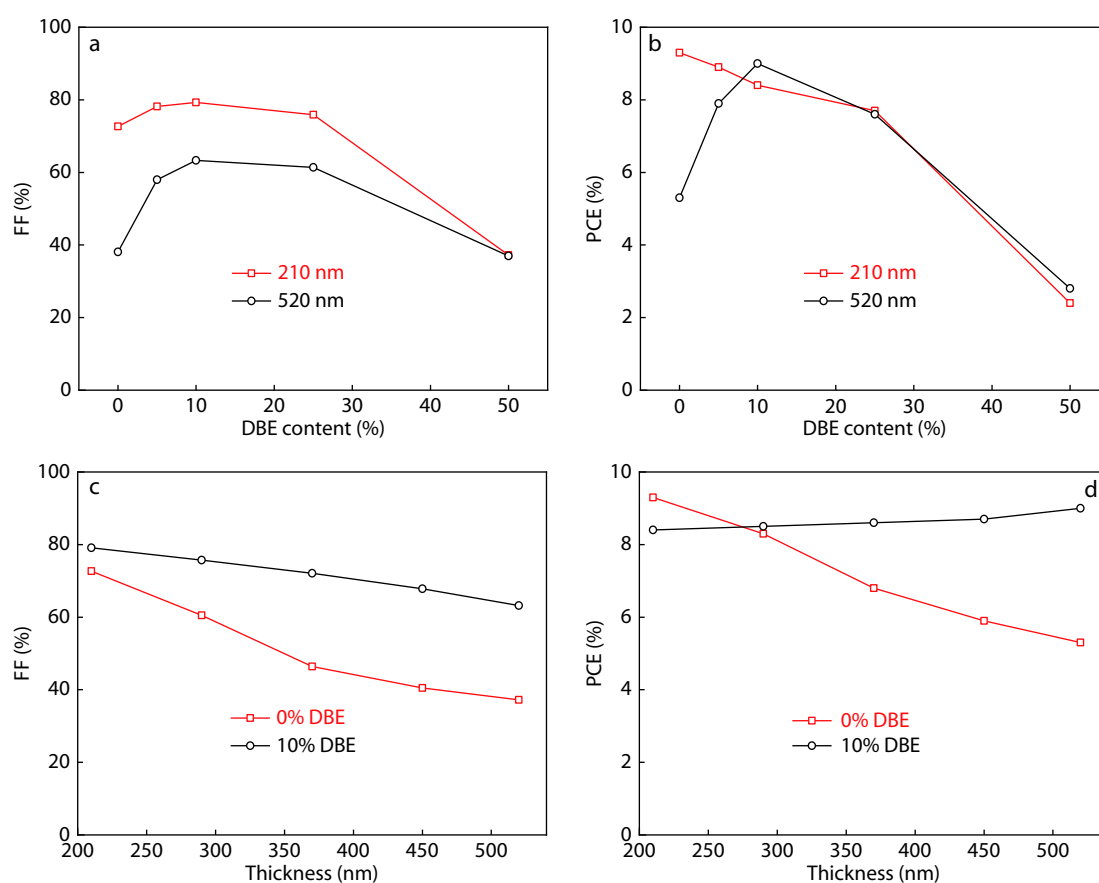


Fig. 2 (a) FF and (b) PCE values of all-PSCs with 210 nm-thick and 520 nm-thick PTzBI-Si:N2200 active layers versus different DBE contents; (c) FF and (d) PCE values versus thickness for all-PSCs based on PTzBI-Si:N2200 films that were processed using CPME with 0% DBE and 10% DBE.

ficant decrease in J_{SC} and FF.

To reveal the effect of using DBE as the solvent additive on the overall performance of the resulting all-PSCs composed of PTzBI-Si:N2200, we investigated charge transfer, carrier transport, and charge recombination of these devices. Charge transfer in the all-PSCs processed using CPME with different DBE contents was examined by conducting the photolumin-

escence (PL) spectroscopy on 500-nm-thick PTzBI-Si:N2200 films.^[51] Quenching of PL emissions from PTzBI-Si and N2200 was more pronounced in the 10% DBE device than in other devices (Figs. 3a and 3b), indicating more effective electron and hole transfers in this device. The efficient PL quenching in the 10% DBE device also implies that the donor (PTzBI-Si) and acceptor (N2200) polymers were mixed on the sub-tens of

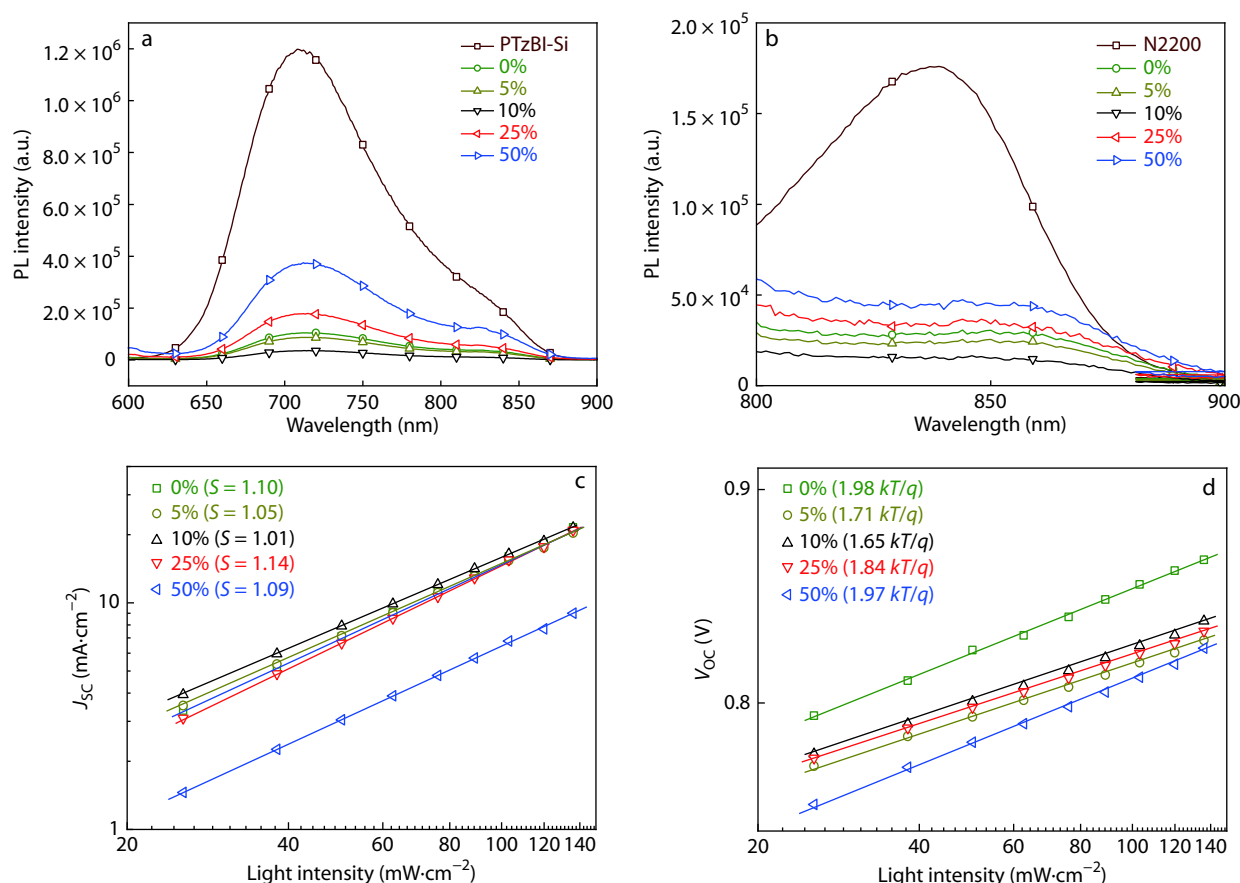


Fig. 3 (a) PL spectra excited at 550 nm; (b) PL spectra excited at 710 nm; (c) J_{SC} and (d) V_{OC} versus light intensity (P_{light}) characteristics for all-PSCs based on 500-nm-thick PTzBI-Si:N2200 films processed using CPME with DBE different contents.

nanometers scale.^[52] Charge carrier mobilities were determined by using the space-charge-limited current (SCLC) method at a film thickness of about 500 nm (Fig. S1 and Table S1 in the electronic supplementary information, ESI). Both hole (μ_h) and electron (μ_e) mobilities increased from 0% DBE to 10% DBE but rapidly decreased upon further increasing the DBE content to 50%. Moreover, the SCLC mobility of 10% DBE all-PSCs was not so sensitive to film thickness compared with that of 0% DBE all-PSCs (Fig. S2, ESI). These observations are consistent with the FF and PCE results of the all-PSCs composed of PTzBI-Si:N2200. The J_{SC} and V_{OC} versus light intensity (P_{light}) characteristics were measured to investigate the charge recombination in all-PSCs processed using CPME with different DBE contents. The power-law dependence between J_{SC} and P_{light} can commonly be expressed as $J_{SC} \propto (P_{light})^S$, where S is approaching to 1 when bimolecular recombination in the device is very weak.^[53,54] The extracted S value of 1.01 approached to 1 for the 10% DBE device (Fig. 3c), implying weaker bimolecular recombination in the 10% DBE device. For V_{OC} versus P_{light} characteristics, a slope of kT/q is anticipated for bimolecular recombination, while a slope of $2kT/q$ stands for the characteristic of monomolecular or trap-assisted Shockley-Read-Hall recombination.^[55] The observed slopes of 1.65 kT/q were close to kT/q for the 10% DBE device (Fig. 3d), implying that monomolecular or trap-assisted Shockley-Read-Hall recombination was effectively suppress-

ed in this device. These observations are in accordance with the high FF and PCE values of the 10% DBE thick-film all-PSCs.

The discrepancy in photovoltaic performance, charge carrier mobility, and recombination characteristics can be correlated to huge changes in the nano-morphology of the 500-nm-thick PTzBI-Si:N2200 films. The topographies of the 500-nm-thick PTzBI-Si:N2200 films processed using CPME with different DBE contents were probed by atomic force microscopy (AFM). The surface topographies of these thick films showed an increased root-mean-square values with increasing DBE content (Figs. 4a–4e), implying that excessive DBE content in CPME would result in side effects to the interfacial contacts. The domain size of the phase separation in these thick films was obtained by conducting resonant soft X-ray scattering (RSOXS), and the results are presented in Fig. 4(f). Upon increasing the DBE content from 0 to 10%, the domain space resolved from the RSOXS profiles decreased dramatically from 157.6 nm to 52.3 nm. Further increasing the DBE content to 50%, the domain size increased significantly to 245 nm (Fig. S3a, in ESI). Such a small phase separation of the 10% DBE thick film is favorable for charge transport and leads to less pronounced bimolecular charge recombination losses, resulting in significantly enhanced FF and thus overall photovoltaic performance.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was employed to probe the molecular orientation morpho-

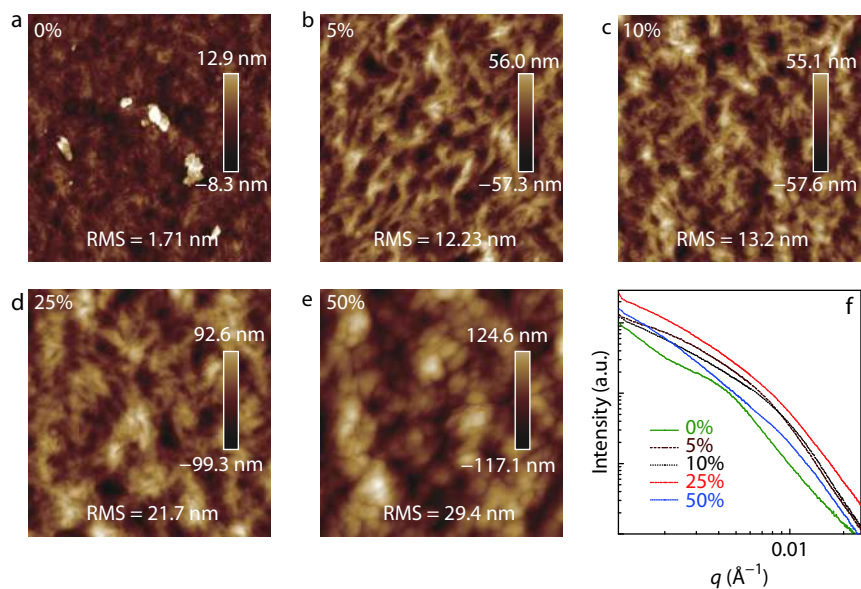


Fig. 4 (a–e) AFM height images ($5 \mu\text{m} \times 5 \mu\text{m}$) and (f) RSoXS profiles of 500-nm-thick PTzBI-Si:N2200 blend films processed using CPME with different DBE contents.

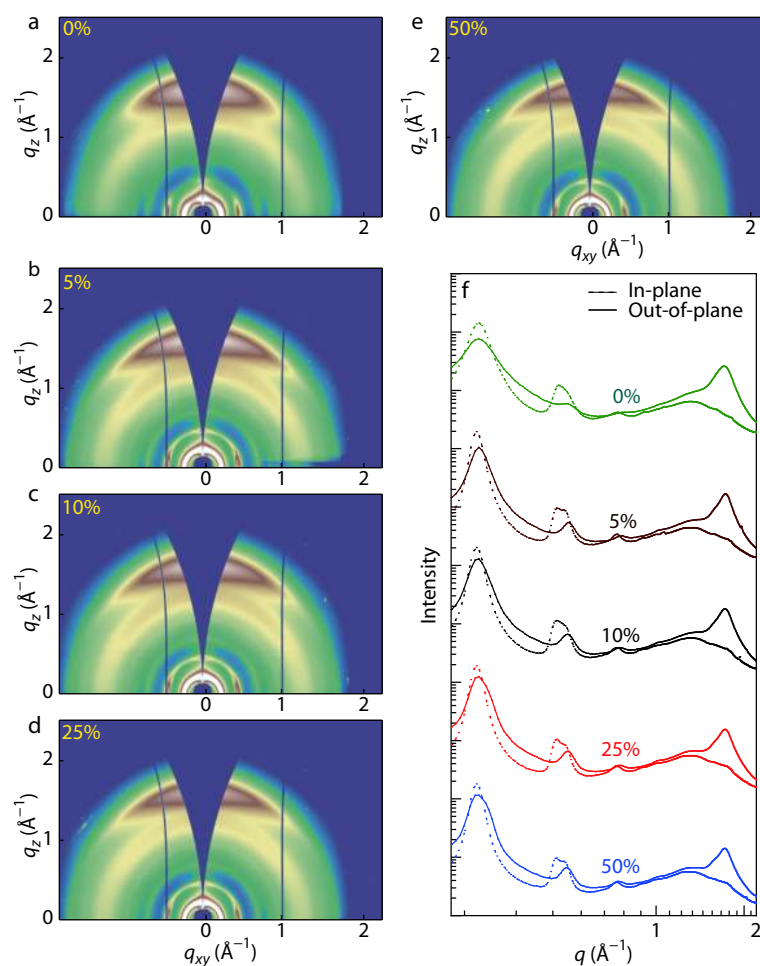


Fig. 5 (a–e) GIWAXS patterns of 500-nm-thick PTzBI-Si:N2200 blended films processed using CPME with different DBE contents; (f) One-dimensional integrated scattering profiles for the blend films.

logy of 500-nm-thick PTzBI-Si:N2200 films processed using CPME with different DBE contents (Fig. 5). The neat PTzBI-Si film demonstrated that π - π stacking peaks, corresponding to the (010) peak, located in the out-of-plane (OOP) direction, while lamellar stacking peaks, corresponding to the (100) peak, located in the in-plane (IP) direction (Figs. S4a and S4b, in ESI); these are similar to those observed in the neat N2200 film (Figs. S4a and S4b, in ESI), indicative of preferential face-on orientation and high crystallinity of these two polymers. PTzBI-Si:N2200 film processed using CPME with different DBE contents could maintain the π - π stacking (010) peak and lamellar stacking (100) peaks of the two neat polymers; however, differences could be observed when changing DBE contents. By increasing the DBE content from 0 to 10%, the π - π stacking distance, which was discerned from GIWAXS profiles, slightly decreased from 3.68 Å to 3.65 Å (Table S2 and Fig. S3b, in ESI); the (010) crystal coherence length (CCL) in OOP slightly enhanced from 1.69 nm to 2.10 nm (Table S2 and Fig. S3c, in ESI), and the (100) CCL in IP increased dramatically from 14.42 nm to 25.12 nm (Table S2 and Fig. S3d, in ESI). CCL was obtained from the Scherrer equation $CCL = 2\pi K/\Delta q$.^[56] Further increasing the DBE content to 50%, the π -

π stacking distance increased slightly to 3.66 Å, the (010) CCL in OOP decreased to 1.64 nm, and the (100) CCL in IP decreased to 20.26 nm. The tighter π - π stacking and improved crystal sizes of polymers in the 10% DBE thick film are favorable for charge transport and thus boost the overall photovoltaic performance.

To validate the versatility of the DBE solvent additive concept in thick-film PSCs, we fabricated devices based on PTzBI:N2200, PTzBI:ITIC, and P2FEhp:Y6, with the chemical structures shown in Fig. S5 (in ESI) and the relevant photovoltaic parameters summarized in Table 2. As anticipated, using DBE as the solvent additive resulted in efficient devices with relatively thick light-harvesting layer for all these combinations. PTzBI:N2200, PTzBI:ITIC, and P2FEhp:Y6 (520 nm thick) devices processed using their respective host solvents with 10% DBE additive achieved superior PCEs of 8.1%, 7.5%, and 10.5%, respectively, as compared to the devices with thickness of about 500 nm processed without DBE. These promising results indicated the huge potential of DBE as a universal green solvent additive, which can be used to facilitate the formation of favorable film morphology of thick-film PSCs toward practical applications.

Table 2 Device parameters of PSCs measured under AM1.5 illumination at 100 mW·cm⁻².

D:A (W:W)	Content of DBE (%)	Thickness (nm)	V _{OC} (V)	J _{SC} (mA·cm ⁻²)	FF (%)	PCE _{avg} (%)	PCE _{max} (%)
PTzBI:N2200 (2:1) ^a	0	210	0.84	15.3 ± 0.4	64.9 ± 0.7	8.2 ± 0.2	8.3
	0	520	0.83	14.1 ± 0.4	38.6 ± 0.9	4.0 ± 0.3	4.3
	10	210	0.83	12.7 ± 0.6	76.4 ± 0.8	7.6 ± 0.4	8.0
	10	520	0.82	15.6 ± 0.3	62.3 ± 0.6	7.9 ± 0.2	8.1
PTzBI:ITIC (1:1) ^b	0	210	0.87	14.9 ± 0.4	66.6 ± 0.5	8.4 ± 0.2	8.6
	0	520	0.85	13.6 ± 0.5	41.3 ± 0.7	4.4 ± 0.3	4.7
	10	210	0.86	12.1 ± 0.6	74.2 ± 0.5	8.4 ± 0.2	7.6
	10	520	0.85	14.2 ± 0.4	63.7 ± 0.9	7.1 ± 0.4	7.5
P2FEhp:Y6 (1:1.2) ^c	0	210	0.89	21.3 ± 0.8	47.5 ± 0.7	8.8 ± 0.3	9.1
	0	520	0.87	18.6 ± 0.7	30.7 ± 0.9	4.7 ± 0.2	4.9
	10	210	0.74	22.5 ± 0.5	68.3 ± 0.6	11.3 ± 0.1	11.4
	10	520	0.70	26.1 ± 0.3	56.9 ± 0.7	10.3 ± 0.2	10.5

^a The host solvent is methyltetrahydrofuran (Me-THF); ^b The host solvent is chlorobenzene (CB); ^c The host solvent is chloroform (CF).

CONCLUSIONS

In conclusion, we discovered a sophisticated green solvent additive DBE to enhance the overall photovoltaic properties of thick-film all-PSCs, which consisted of a wide-bandgap polymer donor PTzBI-Si and a narrow-bandgap polymer acceptor N2200. The resulting all-PSCs processed with CPME in the presence of 10% DBE presented an impressively high PCE of 9% with a PTzBI-Si:N2200 layer thickness of 520 nm, which is clearly superior to the PCE values of all-PSCs processed without DBE. To our knowledge, the PCE of 9.0% achieved with a light-harvesting layer thickness of over 500 nm is the highest PCE value yet reported for thick-film single-junction all-PSCs at such thickness, which implies the tremendous potential of using DBE as a non-halogenated solvent additive for future production by high throughput roll-to-roll technique. The obviously improved PCE is ascribed to the efficient charge transfer, optimized charge transportation, suppressed bimolecular recombination, as well as improved domain spacing and molecular orientation. These observations demonstrated that the DBE solvent additive is marvelously applicable to a range of thick-film PSCs, which

brings about a glimmer of hope to realize the industrialization of PSCs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2356-3>.

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