Environmentally-friendly solvent processed fullerene-free organic solar cells enabled by screening halogen-free solvent additives

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ABSTRACT Though the power conversion efficiencies (PCEs) of organic solar cells (OSCs) have been boosted to 12%, the use of highly pollutive halogenated solvents as the processing solvent significantly hinders the mass production of OSCs. It is thus necessary to achieve high-efficiency OSCs by utilizing the halogen-free and environmentally-friendly solvents. Herein, we applied a halogen-free solvent system (*o*-xylene/1-phenylnaphthalene, XY/PN) for fabricating fullerene-free OSCs, and a high PCE of 11.6% with a notable fill factor (FF) of 72% was achieved based on the PBDB-T:IT-M blend, which is among the top efficiencies of halogen-free solvent processed OSCs. In addition, the influence of different halogen-free solvent additives on the blend morphology and device performance metrics was studied by synchrotron-based tools and other complementary methods. Morphological results indicate the highly ordered molecular packing and highest average domain purity obtained in the blend films prepared by using XY/PN co-solvent are favorable for achieving increased FFs and thus higher PCEs in the devices. Moreover, a lower interaction parameter (χ) of the IT-M:PN pair provides a good explanation for the more favorable morphology and performance in devices with PN as the solvent additive, relative to those with diphenyl ether and *N*-methylpyrrolidone. Our study demonstrates that carefully screening the non-halogenated solvent additive plays a vital role in realizing the efficient and environmentally-friendly solvent processed OSCs.

Keywords: organic solar cells, halogen-free solvent, morphology, high-efficiency

INTRODUCTION

Solution-processable organic semiconductors enable the fabrication of low-cost and flexible electronic devices, such as solar cells, transistors, and light-emitting diodes [1–6]. It is generally known that the high-performance semiconductive materials typically possess planar and rigid conjugated backbones for getting strong intermolecular π - π interaction and flexible non-conjugated substituents for improving solubility [7]. Therefore, these materials usually exhibit good solubility in solvents with strong solvation effects [8,9]. Halogenated solvents, like chloroform (CF), chlorobenzene (CB), are regarded as a series of most commonly used processing solvents for fabricating organic electronic devices [10–13]. However, the pollution caused by the halogenated solvents becomes one of the main obstacles for further large-area device fabrication. Hence, it is of great necessity to remove the halogenated solvents from the fabrication processes. Although the halogen-free solvents are applicable to several polymers in previous reports [14–16], most results obtained from non-halogenated solvent processing are not as high as that those from the halogenated solvent processing. Therefore, achieving high-performance devices using halogen-free solvent systems is still a big challenge in the organic solar cell (OSC) field.

Bulk heterojunction (BHJ) OSC, comprising a p-type semiconductor as the electron donor and an n-type semiconductor as the electron acceptor has been developed rapidly over the years [2,7,9,17–19]. Great efforts have been made to improve the power conversion effi-

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Figure 1 (a) Chemical structures of polymer donor PBDB-T and non-fullerene acceptor IT-M. (b) Halogen-free host solvent *o*-xylene (XY) and three halogen-free solvent additives (DPE, NMP and PN). (c) The configurations of the regular and inverted devices used in this work. (d) Normalized absorption spectra of PBDB-T:IT-M blend film cast from XY, XY/DPE, XY/NMP and XY/PN.

ciencies (PCEs) of OSCs by utilizing novel materials and new processing methods over the past decades [1,20–31]. Recently, high-performance non-fullerene acceptor materials, especially the small-molecule acceptors (SMAs), were successfully developed [32–45]. These SMAs materials exhibit excellent solubility in non-halogen solvents, such as *o*-xylene (XY), anisole and tetrahydrofuran (THF) [46], which have brought the possibility of fabricating high-performance non-fullerene OSCs using non-halogen solvent systems. Although a few groups have reported the application of a particular halogen-free system in processing nonfullerene OSCs before [47–49], the relationships between morphological properties and photovoltaic parameters of the representative non-fullerene OSCs processed by various non-halogen solvent systems have not been well established yet.

In the fabrication of BHJ OSCs, both the donor and acceptor materials should have good solubility in the host solvent, while the solvent additives are often used to fine-tune the morphological properties of the BHJ blend films. Though a large number of studies have been devoted to optimizing the fullerene-based blend morphologies during recent years, such as finding suitable solvent additives and screening the optimal solvent additive content [50–52], research of solvent additive utilization and efficiency is very limited for fullerene-free OSCs. For fullerene-free OSCs, the impact of solvent additives on the molecular packing of non-fullerene acceptors may differ from that of fullerene acceptors due to the totally different molecular

conformation of the two. Therefore, selecting suitable solvent additives is crucial for the development of halogen-free solvents processed non-fullerene OSCs.

In this work, we attempted to investigate the effect of the halogen-free additives on screening the best processing solvent system for a photoactive layer comprising a polymer donor named as poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)-co-(1,3-di(5-thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione)) (PBDB-T) and a non-fullerene acceptor named as IT-M (Fig. 1), which had demonstrated high photovoltaic performance in devices [41,53,54]. Prior to the device study, the solubility of PBDB-T in different halogen-free solvents, such as XY, anisole and THF, was initially tested. The results indicate that PBDB-T shows poor solubility in anisole or THF but can be easily dissolved in XY. In order to avoid using a halogenated additive to fabricate the fullerene-free OSCs, we selected three halogen-free solvents as additives, *N*-methylpyrrolidone (NMP), diphenyl ether (DPE) and 1-phenylnaphthalene (PN), which have been used as solvent additives in the fullerene-based OSCs [14,55,56]. Therefore, in this work, the fullerene-free OSCs based on PBDB-T:IT-M were fabricated with XY as the host solvent, NMP, DPE and PN were selected as the solvent additive to improve the active layer morphology, respectively. When processed by XY/PN as the processing solvent, the fullerene-free OSCs with a conventional device structure demonstrated an optimal efficiency of 11.3%, which could be

improved to 11.6% by adopting the inverted device structure. How the addition of these halogen-free solvent additives affects the morphology of this model system was also explored by the use of grazing incidence wide-angle X-ray scattering (GIWAXS) and resonant soft X-ray scattering (R-SoXS).

EXPERIMENTAL SECTION

Materials

PBDB-T and IT-M were synthesized in our laboratory according to the previous studies [41]. The number average molecular weight (M_n) of PBDB-T was 22 kDa with a polydispersity index (PDI) of 3.3. PFN-Br was purchased from Solarmer Materials (Beijing) Inc. The processing solvents used in the device fabrication processes were purchased from Alfa Aesar. Electrode materials were commercially available products without further purification.

Fabrication and characterization of organic solar cells

The regular OSCs were fabricated with a device architecture of ITO/PEDOT:PSS/PBDB-T:IT-M/PFN-Br/Al. Indium-tin oxide (ITO) substrates with a sheet resistance of $15 \Omega \text{ sq}^{-1}$ were cleaned with detergent water, deionized water, acetone and isopropyl alcohol in an ultrasonic bath sequentially for 10 minutes, and then dried in an oven at 150°C for 30 minutes. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Heraeus Materials, 4083) was spin-coated on ITO, and the ITO glass substrates coated with PEDOT:PSS were transferred to nitrogen-filled glovebox after annealing at 150°C for 15 min. The concentration of PBDB-T:IT-M (1:1; w/w) in XY solution was 10 mg mL^{-1} for the polymer. 1 vol% of solvent additive (DPE, NMP and PN) was added into the blend solution, respectively. The thickness of PBDB-T:IT-M blend film was $\sim 100 \text{ nm}$. The active layer was baked at 100°C for 10 min, and then $\sim 60 \mu\text{L}$ PFN-Br at a concentration of 0.5 mg mL^{-1} in methanol was deposited on the active layer at 3000 rpm for 60 s. The metal electrode was deposited by thermal evaporation of Al (100 nm) through a mask with 4 mm^2 under vacuum at a pressure of $3 \times 10^{-4} \text{ Pa}$. The inverted OSCs were fabricated with a structure of ITO/ZnO/PBDB-T:IT-M/ MoO_3 /Al. The ZnO precursor was prepared by dissolving zinc acetate dihydrate and ethanolamine in 2-methoxyethanol, and the ZnO precursor solution was spin-cast on the top of ITO substrates. The substrates were annealed at 200°C for 1 h [57]. The condition of blend film based on PBDB-T:IT-M in inverted OSCs is the same with that used in the con-

ventional OSCs. The current-voltage curves of devices were measured under 100 mW cm^{-2} standard AM 1.5G spectrum. The spectral mismatch factor was calibrated to be unity by a National Institute of Metrology (NIM) certificated silicon reference cell with a KG3 filter [58]. All external-quantum-efficiency (EQE) curves were measured through the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was also calibrated by monocrystalline silicon solar cell in advance.

Morphology characterizations

GIWAXS [59] and R-SoXS [60] measurements were respectively performed at the beamline 7.3.3, and beamline 11.0.1.2, advanced light source (ALS), Lawrence Berkeley National Laboratory, following the previously established protocols. GIWAXS data were acquired just above the critical angle (0.13°) of the films with a hard X-ray energy of 10 keV, and silver behenate (AgB) was used for geometry calibration. R-SoXS was performed in a transmission geometry with linearly polarized photons under high vacuum ($1 \times 10^{-7} \text{ Torr}$) and a Peltier-cooled (-45°C) charge-coupled device (CCD) (Princeton PI-MTE, 2048 pixels $\times$ 2048 pixels) was used to capture the soft X-ray scattering 2D patterns.

RESULTS AND DISCUSSION

Device performance

To evaluate the photovoltaic performance of PBDB-T:IT-M-based devices processed by adding different halogen-free additives, the OSC devices (Fig. 1c) with a conventional configuration of ITO/PEDOT:PSS/PBDB-T:IT-M/PFN-Br/Al were fabricated, and the PEDOT:PSS and PFN-Br were utilized as the p-type and n-type interlayers, respectively [61]. The weight ratio of PBDB-T and IT-M maintains at 1:1 and the thickness of the active layers is kept at around 100 nm by referring our recent studies [41,54]. Fig. 2a shows the current density-voltage (J - V) characteristics of the optimal devices fabricated using different solvent systems and the corresponding parameters are listed in Table 1.

The device fabricated using neat XY as the processing solvent exhibits an open-circuit voltage (V_{oc}) of 0.940 V, a short-circuit current density (J_{sc}) of 16.3 mA cm^{-2} , a fill factor (FF) of 0.543 and a PCE of 8.32%, which is much lower than those of the devices fabricated by the CB/DIO combination in our recent work [41,54]. When a trace amount (1%, v/v) of DPE or NMP is added as the solvent additive, the J_{sc} is slightly increased, while the FF is in-

Figure 2 (a) J - V and (b) EQE curves of the optimized devices using XY and different solvent additives (DPE, NMP, and PN) as the co-solvent under AM 1.5 conditions, 100 mW cm^{-2} ; (c) photovoltaic parameters (PCE, J_{sc} , V_{oc} , and FF) of PSCs processed using different solvent additives; (d) J_{ph} versus V_{eff} plots of the optimal devices processed using different solvent additives.

Table 1 The photovoltaic parameters of PBDB-T:IT-M-based fullerene-free OSCs processed with different halogen-free solvents

Solvents	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE _{max} ^{a)} (%)	PCE _{avg} ^{b)} (%)
XY	0.940	16.3	0.543	8.32	7.98±0.23
XY/DPE	0.944	16.5	0.603	9.39	9.07±0.25
XY/NMP	0.949	16.8	0.657	10.5	10.0±0.39
XY/PN	0.948	17.0	0.703	11.3	10.9±0.35
XY/PN ^{c)}	0.942	17.1	0.721	11.6	11.3±0.21

a) PCE_{max} is the result of the best-performing device. b) Average PCE values are obtained from over 20 devices fabricated in parallel. c) Using inverted device structure: ITO/ZnO/PBDB-T:IT-M/MoO₃/Al.

creased to 0.603 and 0.657, respectively, hence the PCE can be improved to 9.39% and 10.5%, respectively. When 1% (vol) PN was used as the additive, a high PCE of 11.3% can be achieved, with a V_{oc} of 0.948 V, a J_{sc} of 17.0 mA cm^{-2} , and a notable FF of 0.703, which is almost close to the PCEs of the CB/1% (vol) DIO processed devices. Fig. 2b shows that the EQE spectra of the devices processed by using XY with the additives are slightly higher than that of the device processed by neat XY in the region of 500–700 nm, indicating that the increase of J_{sc} is originated from both the donor and acceptor after adding the solvent additives, especially for 1% PN. The J_{sc} values integrated from the EQE curves agree well with those from J - V measurements. The variations of the photovoltaic parameters of the devices processed by different processing solvents are summarized in Table 1 and Fig. 2c. As depicted in Fig. 2c, the dramatically increased FF is the main

reason for the improved PCE of the devices. In addition, the great decrease of series resistance (R_s) and the increase of shunt resistance (R_{sh}) as shown in Fig. S1 clearly demonstrate that halogen-free solvent mixture (XY/1% PN) is quite suitable for fabricating the high-performance fullerene-free OSCs based on the PBDB-T:IT-M blend system (see Fig. S1 and Table S1).

To further investigate the effect of additive solvents on the photovoltaic behaviors of the devices, the relationships between photocurrent density (J_{ph}) and effective voltage (V_{eff}) of the devices are plotted in Fig. 2d ($J_{ph} = J_L - J_D$, where J_L is the current density under illumination and J_D is the current density in the dark. $V_{eff} = V_o - V_a$, where V_a is the applied voltage and V_o is the voltage at which J_{ph} is zero) [62]. The exciton dissociation probabilities (P_{diss}) were calculated to be 83.8%, 84.8%, 85.6%, and 87.3% for the PBDB-T:IT-M-based devices processed by XY, XY/1%

Figure 3 AFM height (a–d) and phase (e–h) images of PBDB-B:IT-M blend films processed by XY, XY/DPE, XY/NMP and XY/PN, respectively.

DPE, XY/1% NMP and XY/1% PN, respectively, indicating more efficient exciton dissociation and higher electrode charge collection efficiency in the XY/PN-processed devices, which all account for the highest J_{sc} of the device. We further fabricated the inverted devices with a structure of ITO/ZnO/PBDB-T:IT-M/MoO₃/Al using XY/1% PN solvent system, and the best PCE of 11.6% with an improved J_{sc} of 17.1 mA cm⁻² and a remarkably high FF of 0.721 was achieved (see Fig. S2 and Table S2). Notably, the PCE of 11.6% is among the top efficiencies of OSCs fabricated with halogen-free solvents. Moreover, the inverted devices processed by XY/DPE and XY/NMP were also fabricated, and the devices achieved PCEs of 9.79% and 10.7%, respectively, which were slight higher than that of conventional device (see Fig. S2 and Table S2). Note that the molecular weight of the polymer always has great impact on the device performance, when the M_n of PBDB-T is decreased to 15 kDa, the corresponding device processed by XY/PN exhibits a lower PCE of 10.4% with a V_{oc} of 0.950 V, a J_{sc} of 15.1 mA cm⁻², and a FF of 0.726 (see Fig. S3 and Table S3).

Charge mobilities

We also measured the carrier mobilities of the PBDB-T:IT-M blend films processed by XY, XY/1% (vol) DPE, XY/1% (vol) NMP and XY/1% (vol) PN using the space-charge-limited current (SCLC) mode. The measurements were carried out by fabricating the hole-only devices with a structure of ITO/PEDOT:PSS/PBDB-T:IT-M/Au and the electron-only devices with a structure of ITO/ZnO/PBDB-T:IT-M/Al. As shown in Fig. S4 and Table S1, the hole and electron mobilities of the PBDB-T:IT-M blend film processed by XY, were found to be 2.33×10^{-5} and 7.00×10^{-5} cm² V⁻¹ s⁻¹, respectively, which are significantly lower than those of the blend films cast from XY/1% (vol)

DPE, XY/1% (vol) NMP and XY/1% (vol) PN. The XY/PN processed blend films exhibit the highest hole (1.27×10^{-4} cm² V⁻¹ s⁻¹) and electron mobility (3.54×10^{-4} cm² V⁻¹ s⁻¹), respectively. The higher charge mobility and the more symmetric charge transport in the blend film processed by XY/1% (vol) PN could partially explain the improved J_{sc} and FF for the XY/PN-processed devices. As shown in prior studies [63,64], the charge transport and collection in fullerene-free OSCs are largely determined by the morphology of the BHJ layer at various length scales.

Surface morphology

To understand the morphologies of the blend films cast from different halogen-free solvents, we employed atomic force microscopy (AFM) to detect the surface morphological characteristics. As shown in Fig. 3, all these PBDB-T:IT-M-based blend films processed by different halogen-free solvents exhibit uniform surfaces, and the similar root-mean-square roughness values (R_q) of 1.3 ± 0.1 nm are obtained. From all of the height images, small fiber-like aggregations can be observed. These fiber-like features of the blends are ascribed mainly to the PBDB-T, because this polymer has strong aggregation effect in solution and in the solid films, and the similar phenomenon was also observed in our previous reports [41,53,61]. As a result, understanding the performance difference among these blend films requires in-depth characterizations of molecular packing and bulk morphology.

Molecular packing and texture

To compare the molecular packing and texture of the PBDB-T:IT-M blend films processed with different halogen-free solvent systems, GIWAXS measurements were carried out [65,66]. As shown in Fig. 4, the blend films processed with XY, XY/DPE, XY/NMP and XY/PN show

Figure 4 GIWAXS patterns of the blend films processed from (a) XY, (b) XY/DPE, (c) XY/NMP and (d) XY/PN, respectively.

clear lamellar (100) and the π - π stacking (010) peaks. In addition, the blend films processed with XY show comparable out-of-plane (OOP) and in-plane (IP) populations (see Fig. S5), indicative of random and disordered packing. While in the blend films processed with XY/additives, the π - π stacking peaks in the OOP direction are more pronounced than those in the IP direction, which indicates these blend films exhibit preferential face-on orientation with respect to the substrates. Surprisingly, the XY/PN processed films exhibit significantly more ordered π - π stacking and many new scattering peaks. By analyzing the GIWAX patterns of the neat films processed at the same conditions (Fig. S6), we found this new polymorph can be ascribed to the IT-M. As shown in the differential scanning calorimetry (DSC) thermograms (Fig. S7) of the blends processed with different solvents, no clear melting peak is observable up to 320°C of heating, which means all the blends represent highly amorphous features. Understanding of such a complex polymorph and the origin in polymer:small molecule blend requires detailed analysis and is thus outside the scope of the current study. For the blend films processed with XY/DPE, and XY/NMP, the relatively low intensity of both lamellar and π - π stacking reflections are observed. Therefore, with PN present, the SMA in the blend films processed from XY becomes relatively more ordered. This can be verified by the UV-vis absorption spectra (Fig. 1d) of PBDB-T:IT-M blend films

processed from XY, XY/DPE, XY/NMP and XY/PN. As shown in Fig. 1d, the shoulder peak around 700 nm should be attributed to the aggregations of the fullerene-free acceptor because the absorption edge (λ_{edge}) of the PBDB-T film is 690 nm, and the absorption intensity of blend film processed from XY/PN of the shoulder peak centered at ~700 nm is much stronger than the blend films processed from XY, XY/DPE, and XY/NMP, which implies that the fullerene-free acceptor IT-M exhibits enhanced aggregation in the XY/PN processed blend films.

Mesoscale morphology

Furthermore, R-SoXS was employed to study the mesoscale morphology of the PBDB-T:IT-M blends films cast from various halogen-free solvents. Following our previous studies [41], a soft X-ray energy of 283.8 eV was also selected here. Fig. 5a shows the Lorentz-corrected R-SoXS profiles of blend films cast from various halogen-free solvents. All the R-SoXS profiles are dominated by single lognormal distribution and thus yield relative comparisons of long periods (center-to-center domain spacings) and average domain purity, which is approximately the root square of integrated scattering intensity (ISI) of the entire Lorentz-corrected profile over the length scale probed. The assumptions and justification of this methodology are discussed at length in the appendix of Supplementary information. The blend films processed from

Figure 5 Thickness normalized and Lorentz-corrected R-SoXS profiles of (a) of the blend films processed from XY, XY/1% (vol) DPE, XY/1% (vol) NMP and XY/1% (vol) PN, respectively. (b) Plot of the relative ISI of the PBDB-T:IT-M based OSCs as a function of the solvent system.

XY/PN and XY/NMP show a long period of $25 \pm 5 \text{ nm}$, implying an almost unchanged length scale of phase separation. The resembling domain spacings are in agreement with the similar J_{sc} values ($16\text{--}17 \text{ mA cm}^{-2}$) observed. As mentioned earlier, ISI is a good indicator of average domain purity of blend systems. The relative ISI was plotted against the solvent system. We further plot device FF of the OSCs *versus* the relative ISI (here we assigned a value of 1 to the highest ISI) in Fig. S8, and the FF was found to have a strong monotonic correlation with the relative ISI. Generally, a higher ISI leads to more suppressed bimolecular recombination and thus promotes the device FFs. Clearly, the XY/PN processed films show the highest average domain purity, which is very consistent with the highest FF achieved [65,66].

Material:additive interactions

In order to understand the differences in performance and morphology, interactions between IT-M and these solvent additives are estimated based on group additive methods [67]. The results are listed in Table S4. The interaction parameter (χ) of a binary blend system can be evaluated according to the equation $\chi = v(\delta_2 - \delta_1)^2/RT$, where δ_1 and δ_2 are the solubility parameters of IT-M and solvent, respectively, and v is the molar volume of the solvent. According to thermodynamics, the higher the volume normalized interaction parameter (χ/v), the lower the miscibility between IT-M and solvent. The χ/v values of IT-M:DPE, IT-M:NMP, IT-M:PN pairs are 1.3×10^{-4} , 2.1×10^{-4} , 1.0×10^{-4} , respectively. As a result, PN is a more favorable solvent additive for IT-M compared with DPE and NMP. Due to the high boiling point of PN and high miscibility of PN:IT-M, XY/PN processing provides more time and solubility for IT-M to achieve highly ordered packing and high phase purity. These results suggest the

evaluation of material:additive interactions can be potentially applied to pre-screen halogen-free solvent additives. Ultimately, this method established here will be useful to minimize the laborious device optimizations of non-fullerene OSCs.

CONCLUSIONS

In summary, we applied a series of halogen-free solvent additives (DPE, NMP, PN) to process a high-performance fullerene-free blend PBDB-T:IT-M, and the corresponding device performance and morphology are found to be starkly different. Using a new halogen-free solvent combination (XY/PN), a PCE of 11.6% with a V_{oc} of 0.942 V, a J_{sc} of 17.1 mA cm^{-2} , and a FF of 0.721 was achieved in the inverted devices based on PBDB-T:IT-M blend film, which is the highest PCE among fullerene-free OSCs fabricated with halogen-free solvents. In addition, we identified the direct relationships between photovoltaic performance and morphology characteristics in these eco-friendly fullerene-free OSCs by using a combination of AFM, GI-WAXS, and R-SoXS. Lamellar and π - π packings are more ordered and average domain purity is the highest in blend films processed by XY/1% (vol) PN, compared to other solvents. These morphological features collectively result in a highest FF and PCE in the XY/PN-processed devices. Our study demonstrates that carefully selecting the non-halogen solvent additive plays a vital role in realizing highly-efficient environmentally-friendly OSCs. More importantly, the halogen-free solvent:additive combination and screening methodologies reported in this study have the potential to guide the optimization of other nonfullerene OSCs. We believe the quest of eco-friendly solvents and highly soluble material systems in these solvents will ultimately lead to valued OSC products in the near future.

Received 3 June 2017; accepted 20 July 2017;
published online 7 August 2017

- 1 Li G, Zhu R, Yang Y. Polymer solar cells. *Nat Photon*, 2012, 6: 153–161
- 2 Li Y. Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption. *Acc Chem Res*, 2012, 45: 723–733
- 3 Muccini M. A bright future for organic field-effect transistors. *Nat Mater*, 2006, 5: 605–613
- 4 Mei J, Diao Y, Appleton AL, *et al.* Integrated materials design of organic semiconductors for field-effect transistors. *J Am Chem Soc*, 2013, 135: 6724–6746
- 5 Müller CD, Falcou A, Reckefuss N, *et al.* Multi-colour organic light-emitting displays by solution processing. *Nature*, 2003, 421: 829–833
- 6 Halim H, Guo Y. Flexible organic-inorganic hybrid perovskite solar cells. *Sci China Mater*, 2016, 59: 495–506
- 7 Ye L, Zhang S, Huo L, *et al.* Molecular design toward highly efficient photovoltaic polymers based on two-dimensional conjugated benzodithiophene. *Acc Chem Res*, 2014, 47: 1595–1603
- 8 Liu F, Gu Y, Shen X, *et al.* Characterization of the morphology of solution-processed bulk heterojunction organic photovoltaics. *Prog Polymer Sci*, 2013, 38: 1990–2052
- 9 Huang Y, Kramer EJ, Heeger AJ, *et al.* Bulk heterojunction solar cells: morphology and performance relationships. *Chem Rev*, 2014, 114: 7006–7043
- 10 Liu Y, Zhao J, Li Z, *et al.* Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells. *Nat Commun*, 2014, 5: 5293
- 11 Zhang S, Ye L, Zhao W, *et al.* Realizing over 10% efficiency in polymer solar cell by device optimization. *Sci China Chem*, 2015, 58: 248–256
- 12 Li M, Gao K, Wan X, *et al.* Solution-processed organic tandem solar cells with power conversion efficiencies >12%. *Nat Photon*, 2016, 11: 85–90
- 13 Huang J, Carpenter JH, Li CZ, *et al.* Highly efficient organic solar cells with improved vertical donor-acceptor compositional gradient *via* an inverted off-center spinning method. *Adv Mater*, 2016, 28: 967–974
- 14 Zhao J, Li Y, Yang G, *et al.* Efficient organic solar cells processed from hydrocarbon solvents. *Nat Energy*, 2016, 1: 15027
- 15 Zhao W, Ye L, Zhang S, *et al.* A universal halogen-free solvent system for highly efficient polymer solar cells. *J Mater Chem A*, 2015, 3: 12723–12729
- 16 Fan B, Ying L, Wang Z, *et al.* Optimisation of processing solvent and molecular weight for the production of green-solvent-processed all-polymer solar cells with a power conversion efficiency over 9%. *Energy Environ Sci*, 2017, 10: 1243–1251
- 17 Lin Y, Zhan X. Non-fullerene acceptors for organic photovoltaics: an emerging horizon. *Mater Horiz*, 2014, 1: 470–488
- 18 Zhang ZG, Li Y. Side-chain engineering of high-efficiency conjugated polymer photovoltaic materials. *Sci China Chem*, 2015, 58: 192–209
- 19 Nielsen CB, Holliday S, Chen HY, *et al.* Non-fullerene electron acceptors for use in organic solar cells. *Acc Chem Res*, 2015, 48: 2803–2812
- 20 Yao H, Ye L, Zhang H, *et al.* Molecular design of benzodithiophene-based organic photovoltaic materials. *Chem Rev*, 2016, 116: 7397–7457
- 21 Lu L, Zheng T, Wu Q, *et al.* Recent advances in bulk heterojunction polymer solar cells. *Chem Rev*, 2015, 115: 12666–12731
- 22 Yip HL, Jen AKY. Recent advances in solution-processed interfacial materials for efficient and stable polymer solar cells. *Energy Environ Sci*, 2012, 5: 5994
- 23 Fan B, Zhang K, Jiang XF, *et al.* High-performance nonfullerene polymer solar cells based on imide-functionalized wide-bandgap polymers. *Adv Mater*, 2017, 29: 1606396
- 24 Zhang G, Zhang K, Yin Q, *et al.* High-performance ternary organic solar cell enabled by a thick active layer containing a liquid crystalline small molecule donor. *J Am Chem Soc*, 2017, 139: 2387–2395
- 25 Zhao F, Dai S, Wu Y, *et al.* Single-junction binary-blend non-fullerene polymer solar cells with 12.1% efficiency. *Adv Mater*, 2017, 29: 1700144
- 26 Lu H, Xu X, Bo Z. Perspective of a new trend in organic photovoltaic: ternary blend polymer solar cells. *Sci China Mater*, 2016, 59: 444–458
- 27 Yao H, Ye L, Fan B, *et al.* Influence of the alkyl substitution position on photovoltaic properties of 2D-BDT-based conjugated polymers. *Sci China Mater*, 2015, 58: 213–222
- 28 Bin H, Gao L, Zhang ZG, *et al.* 11.4% Efficiency non-fullerene polymer solar cells with trialkylsilyl substituted 2D-conjugated polymer as donor. *Nat Commun*, 2016, 7: 13651
- 29 Bin H, Zhong L, Zhang ZG, *et al.* Alkoxy substituted benzodithiophene-alt-fluorobenzotriazole copolymer as donor in non-fullerene polymer solar cells. *Sci China Chem*, 2016, 59: 1317–1322
- 30 Zhang Z, Li M, Liu Y, *et al.* Simultaneous enhancement of the molecular planarity and the solubility of non-fullerene acceptors: effect of aliphatic side-chain substitution on the photovoltaic performance. *J Mater Chem A*, 2017, 5: 7776–7783
- 31 Zhao W, Zhang S, Hou J. Realizing 11.3% efficiency in fullerene-free polymer solar cells by device optimization. *Sci China Chem*, 2016, 59: 1574–1582
- 32 Lin Y, Zhan X. Oligomer molecules for efficient organic photovoltaics. *Acc Chem Res*, 2016, 49: 175–183
- 33 Lin Y, Wang J, Zhang ZG, *et al.* An electron acceptor challenging fullerenes for efficient polymer solar cells. *Adv Mater*, 2015, 27: 1170–1174
- 34 Lin Y, Zhang ZG, Bai H, *et al.* High-performance fullerene-free polymer solar cells with 6.31% efficiency. *Energy Environ Sci*, 2015, 8: 610–616
- 35 Lin Y, He Q, Zhao F, *et al.* A facile planar fused-ring electron acceptor for as-cast polymer solar cells with 8.71% efficiency. *J Am Chem Soc*, 2016, 138: 2973–2976
- 36 Lin Y, Zhao F, He Q, *et al.* High-performance electron acceptor with thienyl side chains for organic photovoltaics. *J Am Chem Soc*, 2016, 138: 4955–4961
- 37 Wang W, Yan C, Lau T-K, *et al.* Fused hexacyclic nonfullerene acceptor with strong near-infrared absorption for semitransparent organic solar cells with 9.77% efficiency. *Adv Mater*, 2017, doi: 10.1002/adma.2017013081701308
- 38 Meng D, Sun D, Zhong C, *et al.* High-performance solution-processed non-fullerene organic solar cells based on selenophene-containing perylene bisimide acceptor. *J Am Chem Soc*, 2016, 138: 375–380
- 39 Yang Y, Zhang ZG, Bin H, *et al.* Side-chain isomerization on an *n*-type organic semiconductor ITIC acceptor makes 11.77% high efficiency polymer solar cells. *J Am Chem Soc*, 2016, 138: 15011–

- 15018
- 40 Holliday S, Ashraf RS, Wadsworth A, *et al.* High-efficiency and air-stable P3HT-based polymer solar cells with a new non-fullerene acceptor. *Nat Commun*, 2016, 7: 11585
- 41 Li S, Ye L, Zhao W, *et al.* Energy-level modulation of small-molecule electron acceptors to achieve over 12% efficiency in polymer solar cells. *Adv Mater*, 2016, 28: 9423–9429
- 42 Yao H, Cui Y, Yu R, *et al.* Design, synthesis, and photovoltaic characterization of a small molecular acceptor with an ultra-narrow band gap. *Angew Chem Int Ed*, 2017, 56: 3045–3049
- 43 Dai S, Zhao F, Zhang Q, *et al.* Fused nonacyclic electron acceptors for efficient polymer solar cells. *J Am Chem Soc*, 2017, 139: 1336–1343
- 44 Liu Y, Zhang Z, Feng S, *et al.* Exploiting noncovalently conformational locking as a design strategy for high performance fused-ring electron acceptor used in polymer solar cells. *J Am Chem Soc*, 2017, 139: 3356–3359
- 45 Li S, Liu W, Li CZ, *et al.* A simple perylene diimide derivative with a highly twisted geometry as an electron acceptor for efficient organic solar cells. *J Mater Chem A*, 2016, 4: 10659–10665
- 46 Zheng Z, Awartani OM, Gautam B, *et al.* Efficient charge transfer and fine-tuned energy level alignment in a THF-processed fullerene-free organic solar cell with 11.3% efficiency. *Adv Mater*, 2017, 29: 1604241
- 47 Dayneko SV, Hendsbee AD, Welch GC. Fullerene-free polymer solar cells processed from non-halogenated solvents in air with PCE of 4.8%. *Chem Commun*, 2017, 53: 1164–1167
- 48 Ye L, Xiong Y, Yao H, *et al.* High performance organic solar cells processed by blade coating in air from a benign food additive solution. *Chem Mater*, 2016, 28: 7451–7458
- 49 Ye L, Xiong Y, Li S, *et al.* Precise manipulation of multilength scale morphology and its influence on eco-friendly printed all-polymer solar cells. *Adv Funct Mater*, 2017, 48: 1702016
- 50 Lou SJ, Szarko JM, Xu T, *et al.* Effects of additives on the morphology of solution phase aggregates formed by active layer components of high-efficiency organic solar cells. *J Am Chem Soc*, 2011, 133: 20661–20663
- 51 Yao Y, Hou J, Xu Z, *et al.* Effects of solvent mixtures on the nanoscale phase separation in polymer solar cells. *Adv Funct Mater*, 2008, 18: 1783–1789
- 52 Lee JK, Ma WL, Brabec CJ, *et al.* Processing additives for improved efficiency from bulk heterojunction solar cells. *J Am Chem Soc*, 2008, 130: 3619–3623
- 53 Zhao W, Qian D, Zhang S, *et al.* Fullerene-free polymer solar cells with over 11% efficiency and excellent thermal stability. *Adv Mater*, 2016, 28: 4734–4739
- 54 Ye L, Zhao W, Li S, *et al.* High-efficiency nonfullerene organic solar cells: critical factors that affect complex multi-length scale morphology and device performance. *Adv Energ Mater*, 2017, 7: 1602000
- 55 Guo X, Cui C, Zhang M, *et al.* High efficiency polymer solar cells based on poly(3-hexylthiophene)/indene-C70 bisadduct with solvent additive. *Energ Environ Sci*, 2012, 5: 7943–7949
- 56 Choi H, Ko SJ, Kim T, *et al.* Small-bandgap polymer solar cells with unprecedented short-circuit current density and high fill factor. *Adv Mater*, 2015, 27: 3318–3324
- 57 Zhao W, Li S, Yao H, *et al.* Molecular optimization enables over 13% efficiency in organic solar cells. *J Am Chem Soc*, 2017, 139: 7148–7151
- 58 Ye L, Zhou C, Meng H, *et al.* Toward reliable and accurate evaluation of polymer solar cells based on low band gap polymers. *J Mater Chem C*, 2015, 3: 564–569
- 59 Hexemer A, Bras W, Glossinger J, *et al.* A SAXS/WAXS/GISAXS beamline with multilayer monochromator. *J Phys-Conf Ser*, 2010, 247: 012007
- 60 Gann E, Young AT, Collins BA, *et al.* Soft X-ray scattering facility at the advanced light source with real-time data processing and analysis. *Rev Sci Instruments*, 2012, 83: 045110–045110
- 61 Zhao W, Li S, Zhang S, *et al.* Ternary polymer solar cells based on two acceptors and one donor for achieving 12.2% efficiency. *Adv Mater*, 2017, 29: 1604059
- 62 Wu JL, Chen FC, Hsiao YS, *et al.* Surface plasmonic effects of metallic nanoparticles on the performance of polymer bulk heterojunction solar cells. *ACS Nano*, 2011, 5: 959–967
- 63 Bauer N, Zhang Q, Zhao J, *et al.* Comparing non-fullerene acceptors with fullerene in polymer solar cells: a case study with FTAZ and PyCNTAZ. *J Mater Chem A*, 2017, 5: 4886–4893
- 64 Mukherjee S, Proctor CM, Tumbleston JR, *et al.* Importance of domain purity and molecular packing in efficient solution-processed small-molecule solar cells. *Adv Mater*, 2015, 27: 1105–1111
- 65 Mukherjee S, Jiao X, Ade H. Charge creation and recombination in multi-length scale polymer:fullerene BHJ solar cell morphologies. *Adv Energ Mater*, 2016, 6: 1600699
- 66 Ye L, Jiao X, Zhang S, *et al.* Control of mesoscale morphology and photovoltaic performance in diketopyrrolopyrrole-based small band gap terpolymers. *Adv Energ Mater*, 2017, 7: 1601138
- 67 Leman D, Kelly MA, Ness S, *et al.* *In situ* characterization of polymer-fullerene bilayer stability. *Macromolecules*, 2015, 48: 383–392
- Acknowledgements** The authors acknowledge the financial support from the National Natural Science Foundation of China (91333204, 21325419 and 51673201), the Chinese Academy of Sciences (XDB12030200, KJZD-EW-J01), the National Basic Research Program 973 (2014CB643501), and the CAS-Croucher Funding Scheme for Joint Laboratories (CAS14601). GIWAXS/R-SoXS and solubility parameter analysis by Ye L and Ade H were supported by the US Office of Naval Research (ONR) grant N00141512322. DSC data and analysis by Ghasemi M were supported by a Research Opportunity Initiative grant by the UNC General Administration. X-ray data were acquired at beamlines 11.0.1.2, and 7.3.3 at Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under Contract No. DE-AC02-05CH11231. Jiao X, Awartani O and Carpenter J are acknowledged for taking part of the R-SoXS data. Zhu C and Wang C are appreciated for the beamline support.
- Author contributions** Zhao W fabricated and optimized the devices; Li S synthesized the nonfullerene acceptor IT-M; Zhang S synthesized PBDB-T; Liu X and Zhang Y carried out the AFM characterizations. Ye L collected and analysed the R-SoXS and GIWAXS data; Ghasemi M did the DSC measurements; He C provided the solvents and additives; Hou J and Ade H supervised the study; all authors commented on the final paper.
- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Supporting data are available in the online version of the paper.

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筛选非卤溶剂添加剂制备非富勒烯有机太阳能电池

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摘要 虽然近年来有机太阳能电池的能量转换效率已经超过13%,但是加工高效率有机太阳能电池的溶剂大多数是含卤溶剂,这些溶剂体系阻碍了有机太阳能电池的进一步发展。因此,探索使用绿色溶剂制备高效率电池具有重要意义。本文在非卤溶剂邻二甲苯作为主溶剂的前提下,通过筛选不同非卤溶剂作为添加剂制备高效有机太阳能电池,在PBDB-T:IT-M共混材料体系中,取得了11.6%的能量转换效率,该效率是使用非卤溶剂加工有机太阳能电池的最高效率之一。我们通过一系列形貌测试将共混薄膜形貌的相区尺寸,相区纯度以及结晶性等重要形貌参数与器件性能进行关联,这对非富勒烯有机太阳能电池的性能优化具有指导意义。本研究表明,通过细致筛选非卤溶剂添加剂调节共混薄膜的形貌,从而可以获得高性能的有机太阳能电池。