Sifting α,ω -di(thiophen-2-yl)alkanes as solvent additives to boost the photovoltaic performance of the PTB7-Th:PC₇₁BM blend†

Jianhong Gao,^a Wei Wang,^a Chun Zhan,^a Yanqi Hu,^a Shengqiang Xiao,^a Xinhui Lu^b and Wei You^c

With a higher boiling point and much improved solubility for PC₇₁BM, α,ω -di(thiophen-2-yl)alkanes (butane, hexane, octane and decane) were applied as processing solvent additives to fabricate PTB7-Th:PC₇₁BM bulk heterojunction (BHJ) polymer solar cells (PSCs). A large gain in photocurrent was achieved for the devices processed with these α,ω -di(thiophen-2-yl)alkanes as additives. The alkyl chain length of the α,ω -di(thiophen-2-yl)alkanes was found to play an important role in regulating the molecular packing, orientation and crystallinity of crystals within the PTB7-Th:PC₇₁BM blend. Increasing the alkyl chain length from butyl to hexyl and to octyl improved the photovoltaic performance and ordering of film microstructures, whereas the decyl chain based additive led to deteriorated performance and ordering. Among all studied additives, 1,8-di(thiophen-2-yl)octane results in the most optimized PTB7-Th:PC₇₁BM blend with more uniform polymer crystals with better crystallinity and improved stacking of PC₇₁BM, thereby leading to the most enhanced power conversion efficiency of 9.87% when compared with the reference device (8.65%) processed with 1,8-diiodooctane (DIO). In addition, the device processed with 1,8-di(thiophen-2-yl)octane showed improved stability. These results demonstrate the potential of 1,8-di(thiophen-2-yl)octane as a new solvent additive to realize high-performance PSCs.

Received 19th July 2018
Accepted 21st September 2018

DOI: 10.1039/c8ta06989a

rsc.li/materials-a

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) based on an intimate blend of a polymer donor and an electron acceptor have been considered as a prospective photoelectric conversion technology because of cost-effective processing.^{1–4} Further increase in power conversion efficiencies (PCEs) of PSCs has been achieved under design principles derived from fundamental correlations between the molecular structure, device interfaces, morphology, and processing conditions. A record PCE of up to 12% for the polymer:fullerene blend and 14% for the polymer:nonfullerene small molecule acceptor blend has been recently reported.^{5–9} Given that the active layer of PSCs is

a physical blend of (polymeric) donors and (molecular) acceptors, proper control and optimization of the morphology of the active layer is critical to high device performance.¹⁰ For example, control of molecular stacking in the solid state for the active layer has been recognized as a grand challenge and even as important as the synthesis of novel active materials and device interfacial engineering.¹¹ Unfortunately, the optimization of solid-state packing of the active materials within a BHJ blend has been very much based on trial and error. Moreover, the optimized morphology for a given BHJ blend to reach the maximum performance is largely material-dependent. Among various morphology control strategies for BHJ blends in PSCs, the use of solvent additives during film processing has attracted a great amount of attention since only a very tiny amount of such additives can significantly improve the overall device performance.^{12–18} In fact, the crystalline structure and the phase-separated networks of the donor and acceptor within a specific BHJ blend can be exquisitely adjusted and optimized with these solvent additives, leading to dramatically enhanced PCEs. For example, 1,8-diiodooctane (DIO) has proven to be one of the most efficient and universal solvent additives for BHJ PSCs.^{15,19–21} Due to its much higher boiling point than the main processing solvents (*e.g.*, *o*-dichlorobenzene and *o*-DCB) and its selective solubility toward the donor or acceptor components in the BHJ blend, DIO allows the soluble component such as the acceptor of PC₇₁BM to form ordered self-organization, resulting

^aState Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, P. R. China. E-mail: shengqiang@whut.edu.cn

^bDepartment of Physics, Chinese University of Hong Kong, Hong Kong, P. R. China. E-mail: xhlu@phy.cuhk.edu.hk

^cDepartment of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, USA. E-mail: wyou@unc.edu

† Electronic supplementary information (ESI) available: Detailed information on device fabrication and characterization, performance optimization, typical *J*-*V* curves with various volume ratios of additives, the absorption spectra of optimized blend films, tapping mode AFM images, and the evolution of photovoltaic parameters of PSC devices processed with DIO and DTO as a function of storage time in a glove box. See DOI: 10.1039/c8ta06989a

in the desired phase separation between the donor and acceptor components during the prolonged film drying process. However, the DIO residue in BHJ blend films appeared vulnerable to degradation due to the generation of iodides even without light illumination. This degradation of DIO led to a performance decay by deteriorating the film morphology, indicating its ‘double-edged’ sword influence on device performance.²² Thus, it is of interest to design and discover innovative solvent additives to replace DIO, aiming to not only enhance the device performance by optimizing the morphological structure of the BHJ blend but also maintain the stability of additives and the overall device.

As stated earlier, a successful solvent additive typically has a higher boiling point and differential solubility towards the two active components.²¹ Since DIO does very well on these two fronts, we intended to modify the structure of DIO. The main issue with DIO, as stated earlier, is its terminal iodides. Thus, we decided to replace them with thiophene units to improve the chemical stability of the resulting additives in comparison with DIO, which would also offer the improved solubility of fullerene derivatives *via* donor–acceptor interactions. On the other hand, the octane based DIO was successfully filtered out as the most efficient one from its analogues with varied alkyl chain length, indicating the importance of an appropriate alkyl chain for a successful solvent additive.¹⁹ Taking into account that the alkyl chain length could also play an important role in influencing the film microstructure, therefore, we also want to vary the chain length between our proposed additives terminated with thiophene units. We then synthesized a series of α,ω -di(thiophen-2-yl)alkanes with $n = 4, 6, 8$, and 10 saturated carbon atoms (molecular structures are presented in Chart 1). As shown in Table 1, the boiling point of 1,4-di(thiophen-2-yl)butane (DTB, $n = 4$) was found to be 319.7°C in a standard atmosphere, very close to that of DIO (332.5°C). With the increasing length of alkyl chains in α,ω -di(thiophen-2-yl)alkanes, the boiling point significantly increases to 370.1°C (DTH, $n = 6$), then gradually to 397.7°C (DTO, $n = 8$), and to 404.2°C (DTD, $n = 10$). In this work, we chose the PTB7-Th:PC₇₁BM blend as

Table 1 Boiling points of the solvent additives in this work and the solubility of PTB7-Th and PC₇₁BM in them

Additive	Boiling point ^a at 1 atm ($^\circ\text{C}$)	Solubility of PTB7-Th (mg mL^{-1})	Solubility of PC ₇₁ BM (mg mL^{-1})
DIO	332.5	—	100 ± 10
DTB	319.7	—	260 ± 10
DTH	370.1	Trace	300 ± 10
DTO	397.7	Trace	300 ± 10
DTD	404.2	Trace	310 ± 10

^a Calculated from Advanced Chemistry Development (ACD/Labs) Software V11.02.

the representative BHJ blend platform due to its superior device performance in polymer:fullerene PSCs to evaluate these α,ω -di(thiophen-2-yl)alkanes as additives. We discovered that the solubility of PC₇₁BM at room temperature in these α,ω -di(thiophen-2-yl)alkanes was improved by 2–3 fold compared with the solubility of PC₇₁BM in DIO (*i.e.*, $100 \pm 10 \text{ mg mL}^{-1}$, Table 1), likely due to the intimate interactions of terminal thiophenes with PC₇₁BM. Interestingly, PTB7-Th was found to be essentially insoluble in DTB and DIO, while it was soluble at a trace level in DTH, DTO, and DTD. Further investigation of using α,ω -di(thiophen-2-yl)alkanes as solvent additives during the processing of PTB7-Th:PC₇₁BM BHJ solar cells disclosed that the alkyl chain length of the new solvent additive also has a noticeable impact on the device performance, with (coincidentally) the octane based new additive demonstrating the highest improvement in device performance.

2. Experimental

2.1 Materials

The donor polymer PTB7-Th was synthesized according to the previously reported method.²³ The acceptor [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM, >99%, EL device grade) was

Chart 1 (a) Schematic representation of the PSC structure, (b) chemical structures of PTB7-Th and PC₇₁BM, and (c) chemical structures of additives including DIO, DTB, DTH, DTO, and DTD.

purchased from Solenne. The additives of α,ω -di(thiophene-2-yl)alkanes were synthesized according to the literature.²⁴ Other chemicals and materials were purchased from Energy Chemical and J&K.

2.2 Grazing incidence wide-angle X-ray scattering (GIWAXS) measurement

GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus 3R 300K detector. The incidence angle is 0.2°.

2.3 Fabrication and characterization of polymer solar cells

Detailed information on the fabrication and characterization of polymer solar cells can be found in the ESI.†

3. Results and discussion

3.1 Photovoltaic properties

As indicated in Chart 1a, an inverted device architecture of glass/ITO/ZnO(30 nm)/PTB7-Th:PC₇₁BM/MoO₃(8 nm)/Ag(100 nm) was fabricated and tested under simulated AM 1.5G solar illumination. The weight ratio of PTB7-Th and PC₇₁BM was fixed at 1 : 1.5 according to previous reports.²³ The optimal amount of α,ω -di(thiophen-2-yl)alkanes as additives was found to be ~7% in volume to the solvent of *o*-DCB (details of device optimization are presented in Fig. S1 and Table S1,† together with the reference DIO device). Fig. 1 shows the typical *J*-*V* curves recorded under simulated AM 1.5G solar irradiation from optimized devices processed with these additives (*i.e.*, α,ω -di(thiophen-2-yl)alkanes and DIO) and their corresponding external quantum efficiency (EQE) spectra. The detailed device characteristics (open circuit

voltage, V_{oc} , short circuit current, J_{sc} , and fill factor, FF) are compiled in Table 2. The DTB device shows an optimized PCE of 8.76%, similar to that of the DIO device (8.65%). As the alkyl chain length increases, the PCE is further enhanced to 9.64% (DTH) and 9.87% (DTO). However, the DTD based device only shows a notably reduced efficiency (8.07%).

A closer look at individual device parameters (V_{oc} , J_{sc} and FF) in Table 2 discloses the notable difference among devices processed with different solvent additives. While the values of V_{oc} do not show much difference among all devices, the values of J_{sc} for devices processed with these new thiophene-terminated additives are noticeably higher than that of the device processed with DIO. On the other hand, as the alkyl chain length increases from butane (DTB) to octane (DTO), the value of J_{sc} continues to increase, with the highest value of 20.78 mA cm⁻² appearing for the devices processed with DTO, a 20% increase compared with that of the devices processed with DIO. However, further increasing the alkyl chain length to decane (DTD) leads to a plummet of the J_{sc} to 18.22 mA cm⁻², which is still higher than that of the DIO device. On the other hand, there is no clear trend for the values of FF, though the DTD device shows the lowest FF (54.70%).

These results demonstrate that the alkyl chain length of these new processing additives plays an important role in affecting the device performance. The highest overall efficiency (close to 10%) of the DTO device is mainly attributed to the much improved J_{sc} . The EQE spectra of these devices were also measured to disclose how the photo-induced currents response within the BHJ blends processed with these additives (Fig. 1b). All devices exhibit broad EQE responses from 300 to 820 nm, and the cell containing the DTO additive presents the highest EQE value of approximately 78% between 650 and 750 nm, suggesting that DTO could have a favourable impact on optimizing the film morphology. In contrast, the DIO device presents lower EQE responses, only reaching 65% in the same range, corroborating the relatively lower J_{sc} of the DIO device. Note that the J_{sc} values obtained under AM 1.5 G irradiation match well with the J_{sc} values obtained from the integration of photoresponse from the EQE spectra for all devices (Fig. S2†).

3.2 Charge generation, transport and recombination

To unravel the origin of the trend of J_{sc} values with the use of α,ω -di(thiophen-2-yl)alkanes, we probed the charge generation and extraction properties by measuring the responses of the photocurrent density (J_{ph}) to the effective voltage (V_{eff}). The J_{ph} is given by $J_{ph} = J_L - J_D$, where J_L and J_D represent the photocurrent densities under illumination and in the dark, respectively. V_{eff} is defined as $V_{eff} = V_0 - V_{appl}$, where V_0 is the built-in voltage when J_{ph} equals zero and V_{appl} is the applied voltage.²⁵ As shown in Fig. 2a, the J_{ph} can reach saturation at a high V_{eff} of 1.3 V and above for all devices, suggesting that the photogenerated excitons can be dissociated and collected at the corresponding electrodes effectively. We thus calculated the maximum photoinduced charge carrier generation rate (G_{max}) via the equation $G_{max} = J_{ph,sat}/qL$, where $J_{ph,sat}$ is the saturated photocurrent density, q is the elementary charge, and L is the

Fig. 1 (a) Typical current density–voltage (*J*-*V*) curves and (b) EQE and integrated J_{sc} curves of PTB7-Th:PC₇₁BM blends processed with DIO and α,ω -di(thiophen-2-yl)alkanes.

Fig. 2 (a) Photogenerated current density versus effective voltage curves under AM 1.5G illumination; (b) dependence of J_{sc} on light intensity; (c) dependence of V_{oc} on light intensity; (d) hole and electron mobility of devices processed with various additives in this work.

thickness of the corresponding active layer. The devices processed with the additives exhibit slightly increased values of G_{max} from DTB ($1.16 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$) and DTH ($1.18 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$) to DTO ($1.20 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$), all of which are higher than that of the DIO device ($1.08 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$). In contrast, the DTD device shows a noticeably decreased value of G_{max} ($1.05 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$). These results indicate that the improved $J_{ph, sat}$ and G_{max} for the DTO device could offer more photogenerated excitons and dissociated charge carriers.

We next investigated the dependency of J_{sc} and V_{oc} on the incident light intensity to evaluate charge recombination when applying these processing additives. Fig. 2b shows the logarithmic plots of J_{sc} as a function of the light intensity by fitting to the power law of $J_{sc} \propto (P_{light})^\alpha$.^{25,26} A slope (α) close to unity would imply weak bimolecular recombination, and more free charges can be swept out and collected at the corresponding electrodes prior to recombination. As for the devices processed with thiophene-terminated additives, except that the DTD device shows a relatively lower α value (0.977), other devices exhibit high α values: 0.985 for the DTB device, 0.989 for the DTH device and 0.990 for the DTO device. In particular, the α value of the DTO device is closer to unity when compared with that of the DIO device (0.986), indicating that the DTO device suppresses the bimolecular recombination more effectively. We also studied the monomolecular recombination under open circuit conditions within all devices by treating V_{oc} as a function of P_{light} following the equation of $V_{oc} \propto (nk_B T/q) \ln(P_{light})$, where k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$) and T is the temperature in Kelvin.²⁷ It has been demonstrated that monomolecular recombination (e.g., trap assisted recombination) is gradually involved in addition to bimolecular recombination when the value of n increases beyond 1 and approaches 2. As shown in Fig. 2c, the DTB device

presents a relatively higher n of 1.13, while the device of DTH ($n = 1.03$) shows almost an identical value to the DTO ($n = 1.02$), suggesting that monomolecular recombination is more suppressed in the latter two devices. The largest n of 1.35 for the DTD device indicates the more severe involvement of monomolecular or trap-assisted recombination in the DTD device. For reference, the DIO device presents an n of 1.09. The significantly suppressed charge recombination (bimolecular and monomolecular recombination) suggests more efficient charge transport within the DTH and DTO devices.

We further measured the hole (μ_h) and electron (μ_e) mobility using the space charge limited current (SCLC) method. The hole- and electron-only devices were fabricated with the configurations of ITO/PEDOT:PSS (40 nm)/active layer/ MoO_3/Ag and ITO/ ZnO (30 nm)/active layer/ Ca/Al , respectively. As shown in Fig. 2d and S3,[†] the average hole mobility was determined to be 1.38, 1.57, 3.01, 3.08 and $1.09 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while the average electron mobility was 1.08, 1.02, 2.31, 2.37 and $0.68 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table S2[†]) for the DIO, DTB, DTH, DTO and DTD processed devices, respectively. As expected, an increasing tendency of both the μ_h and μ_e can be observed from DTB and DTH to DTO, and lowest mobility values were observed with the DTD processed device. The DTO processed devices exhibit improved hole and electron mobility compared with the DIO-processed one, partly explaining the higher J_{sc} for the DTO device. In short, the DTO processed devices have presented improved charge generation and transport efficiency with suppressed charge recombination, facilitating the enhancement of J_{sc} and FF over the devices processed with the other thiophene-terminated additives. All these desirable features of the DTO device contrast with those obtained in the DTD device, explaining the low J_{sc} and FF for the latter device.

3.3 Morphology of the BHJ blend films

Probing the surface morphology of the blend films processed with α,ω -di(thiophen-2-yl)alkanes and DIO *via* atomic force microscopy (AFM) did not reveal much difference (Fig. S4†). We then applied grazing incidence wide-angle X-ray scattering (GIWAXS) to investigate the effect of these additives on the molecular packing, orientation and crystallinity of crystals within the PTB7-Th:PC₇₁BM blend films. Among all the blend films processed with thiophene-terminated additives, DTB, DTH and DTO processed BHJ blends clearly exhibit lamellar diffractions along both the in-plane (IP) and out-of-plane (OOP) directions, similar to those observed for the DIO processed BHJ blend. A diffraction peak corresponding to IP (100) lamellae at $q_r = 0.29 \text{ \AA}^{-1}$ (d spacing of 21.66 Å) and a diffraction peak corresponding to OOP (010) π - π stacking diffraction at $q_z = 1.67 \text{ \AA}^{-1}$ (d spacing of 3.76 Å) were observed for the DTB processed BHJ blend. Meanwhile, the OOP (100) diffraction at a q_z of $0.32 \text{ \AA}^{-1}$ (d spacing of 19.62 Å) with less crystallinity was also observed. These results indicate a typical bimodal molecular packing of PTB7-Th with preferential face-on orientation in the DTB processed BHJ blend. Interestingly, with the increase of alkyl chain length from DTB and DTH to DTO, we observe that the IP (100) diffraction peak of PTB7-Th slightly shifts towards larger q vector with decreased lamellar stacking distance ($0.29 \text{ \AA}^{-1}$ for DTB-, $0.30 \text{ \AA}^{-1}$ for DTH- and $0.31 \text{ \AA}^{-1}$ for DTO-processed BHJ blends) while the q vector of the OOP (100) peaks remains unchanged (Table S3†). The end result is that the spacings of both the IP and OOP (100) lamellae become comparable to each other in the DTO blend, suggesting the transformation of the bimodal molecular packing in the DTB and DTH processed blends to a uniform one in the DTO blend. Furthermore, the intensity of the OOP (100) diffraction slightly increases from

DTB and DTH to DTO, indicating slightly improved crystallinity of edge-on oriented PTB7-Th crystals. Such molecular packing evolution could be responsible for the improved charge generation and transport in the DTO processed device over the DTB and DTH processed ones, leading to an increased J_{sc} and FF in the DTO processed devices. The DIO processed reference blend shows the IP (100) lamellae diffraction at a lower q_r around $0.28 \text{ \AA}^{-1}$ (a longer d spacing of 22.43 Å) with no obvious corresponding detectable OOP (010) π - π stacking. Finally, we also observed typical yet stronger and more ordered PC₇₁BM diffraction peaks at $\sim 1.34 \text{ \AA}^{-1}$ with a d spacing value of 4.68 Å along the IP direction in the DTO processed BHJ blend than those observed in the films processed with other additives, attributed to an improved self-assembly ability of PC₇₁BM in the DTO processed BHJ blend.

In contrast, for the BHJ blend processed with DTD, no obvious diffraction peaks corresponding to crystal lamellae and/or π - π stacking were observed except the diffraction from the relatively weak PC₇₁BM aggregates, indicating the strong influence of the DTD additive on the organization of both PTB7-Th and PC₇₁BM in the blend. Furthermore, a rather unique scattering at $\sim 2.5 \text{ \AA}^{-1}$ was observed in the GIWAXS pattern of the DTD blend (Fig. 3a), which is likely to be due to the amorphous ring that originated from the aggregation of DTD residue in the BHJ blend. We noticed that the BHJ blend processed with DTD took much longer time to dry (by solvent annealing after spin-coating) than the BHJ blends processed with the other additives in this study, which would likely leave more residues of the DTD additive and help explain the much deteriorated device performance compared with the BHJ blends processed with DTB, DTH and DTO.

Although the much improved J_{sc} of the DTO processed device can be ascribed to the synergistic contribution of the thicker

Fig. 3 (a) 2D GIWAXS patterns and (b) in-plane (IP) and out-of-plane (OOP) scattering profiles for PTB7-Th:PC₇₁BM blend films with various additives in this work.

film for more light absorption and suppressed charge recombination compared with the DIO processed reference device, the slight decrease ($\sim 6\%$) of FF for the DTO processed device relative to that of the DIO reference device remains unclear. Given the fact that the BHJ film processed with DTO is $\sim 12\%$ thicker than that from DIO, we suggest that the increased bulk resistance contributes to the slight decrease of FF; in addition, the likely different interfacial morphologies between the electrodes and the active layer for these two different additive processed devices could also contribute.^{28,29}

Fig. 4 Photoluminescence spectra of neat PTB7-Th film and PTB7-Th:PC₇₁BM blends processed with DIO and α,ω -di(thiophen-2-yl)alkanes excited at 688 nm. The region of the spectra circled with a dotted gray line was amplified 15 times as indicated.

Fig. 5 PCEs of the PTB7-Th:PC₇₁BM PSCs processed with DIO and DTO as a function of storage time in a nitrogen-filled glove box.

Given the fact that the alkyl chain length of α,ω -di(thiophen-2-yl)alkanes plays an important role in the BHJ blend morphology, the fluorescence quenching efficiency of PTB7-Th in the BHJ blends was detected to further investigate the efficiency of exciton quenching. As shown in Fig. 4, a quenching efficiency of 96.4%, 96.9%, 97.6%, 97.8%, and 94.1% was obtained for the BHJ blends processed with DIO, DTB, DTH, DTO and DTD, respectively. The increasing exciton quenching efficiency from DTB and DTH to DTO and the slight decrease in the quenching efficiency of DTD correlate well with the above-analysed device performance and film microstructure. The quenching efficiency of the DTO device almost reaches unity, indicating the most efficient photo induced electron transfer from PTB7-Th to PC₇₁BM. This result can be ascribed to the more optimized phase separation between the donor and the acceptor adjusted by DTO than by DIO and further explains the highest J_{sc} of the corresponding solar cell device processed with DTO.

3.4 Device stability

Device stability becomes increasingly important for PSCs besides the PCE. Since the highest PCE was obtained from the DTO processed device, we preliminarily explored the stability of the PTB7-Th:PC₇₁BM devices processed with the champion additive of DTO as a function of the storage time in a nitrogen-filled glove box, together with that of the reference DIO devices. Fig. 5 presents the efficiency stability comparison between the DTO and DIO processed devices over 35 days. The time-dependent photovoltaic parameters J_{sc} , V_{oc} and FF are depicted in Fig. S6† and the average performances are listed in Table S4.† The average starting PCE of 8.59% attenuated to 5.83% with a 33% decrease for the DIO processed device stored in a nitrogen-filled glove box for 35 days. In contrast, during the same period, the average PCE of the DTO processed device retained $\sim 87\%$ of the original value (9.82%). Interestingly, we found that only the J_{sc} and FF exhibited a slight decrease during the period for the DTO processed device with V_{oc} being essentially unchanged. In contrast, a simultaneous decrease of J_{sc} , V_{oc} and FF was observed for the DIO processed device, which could be ascribed to the formation of fullerene-iodide radicals caused by the iodides from degraded DIO residues.²² These results indicate a better stability of the device processed with iodine-free DTO than the DIO processed one under a nitrogen atmosphere resulting from the higher chemical stability of DTO than DIO, indicating the advantage of replacing iodine atoms with terminated thiophenes in this work.

Table 2 Maximum photovoltaic parameters of the PTB7-Th:PC₇₁BM BHJ devices processed with solvent additives (α,ω -di(thiophen-2-yl)alkanes and DIO) in this study under AM 1.5G illumination (parenthesized are the average values and standard deviations over 15 devices)

Additive	Film thickness (nm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
DIO	103 $\pm$ 2	0.796 (0.789 $\pm$ 0.007)	17.25 (17.01 $\pm$ 0.29)	62.85 (62.54 $\pm$ 0.73)	8.65 (8.51 $\pm$ 0.18)
DTB	110 $\pm$ 2	0.782 (0.776 $\pm$ 0.006)	19.61 (19.38 $\pm$ 0.25)	56.80 (56.20 $\pm$ 0.92)	8.76 (8.59 $\pm$ 0.18)
DTH	115 $\pm$ 2	0.803 (0.799 $\pm$ 0.005)	20.43 (20.15 $\pm$ 0.32)	59.20 (58.62 $\pm$ 1.03)	9.64 (9.42 $\pm$ 0.25)
DTO	115 $\pm$ 2	0.805 (0.801 $\pm$ 0.005)	20.78 (20.51 $\pm$ 0.30)	59.43 (58.70 $\pm$ 0.75)	9.87 (9.68 $\pm$ 0.20)
DTD	117 $\pm$ 2	0.806 (0.800 $\pm$ 0.008)	18.22 (18.01 $\pm$ 0.23)	54.70 (54.30 $\pm$ 0.87)	8.07 (7.93 $\pm$ 0.14)

On the other hand, in spite of the fact that the stability of the DTO device is better than that of DIO under a nitrogen atmosphere, the decrease in the trend of photovoltaic performance is still observable, suggesting the existence of a degrading mechanism different from that of DIO. The question may be raised on how this happened providing that DTO is more stable. We suggest that the decrease of device performance could be caused by the local accumulation of DTO residue, which could deteriorate the optimized film morphology. Such speculation arises from the observation of the amorphous scattering in GIWAXS patterns (Fig. 3a) that originated from the possible aggregation of DTD residue in its BHJ blend, which greatly led to the decreased device performance as outlined in Table 2. The residue of DTO and DTD in the BHJ blend is possible because their boiling point and the optimized ratio to the processing solvent are much higher than those of DIO.

4. Conclusions

In summary, a series of α,ω -di(thiophen-2-yl)alkanes were used as solvent additives to process the state-of-the-art PTB7-Th:PC₇₁BM solar cell device. These solvent additives can provide fine control of the BHJ blend morphology by influencing molecular packing during film formation. The chain length of alkanes was found to have a pronounced effect on the molecular organization of the donor and acceptor materials within the BHJ blend. Among all additives studied in this work, 1,8-di(thiophen-2-yl)octane results in devices with the most optimized photovoltaic performance and film ordering over the other α,ω -di(thiophen-2-yl)alkanes and the reference additive DIO. The maximum PCE can be improved from 8.65% with DIO as a reference to 9.87% with 1,8-di(thiophen-2-yl)octane, mainly due to a large gain of short circuit current, which can be attributed to the enhanced organization of the donor and acceptor crystals within the PTB7-Th:PC₇₁BM BHJ blend. Furthermore, the lifetime of the device processed with 1,8-di(thiophen-2-yl)octane significantly increased in comparison with that of the DIO-based device in a nitrogen-filled glove box without encapsulation. All these strongly support that our newly created solvent additive, 1,8-di(thiophen-2-yl)octane, is a very promising candidate as a processing additive for PSCs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

S. Xiao acknowledges the support from the National Natural Science Foundation of China (21673170) and the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing (2017-KF-9, 2018-KF-3).

Notes and references

- 1 L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao and L. Yu, *Chem. Rev.*, 2015, **115**, 12666.
- 2 H. Kang, G. Kim, J. Kim, S. Kwon, H. Kim and K. Lee, *Adv. Mater.*, 2016, **28**, 7821.
- 3 I. Olle, *Adv. Mater.*, 2018, **30**, 1800388.
- 4 A. Wadsworth, M. Moser, A. Marks, M. S. Little, N. Gasparini, C. J. Brabec, D. Baran and I. McCulloch, *Chem. Soc. Rev.*, 2018, DOI: 10.1039/c7cs00892a.
- 5 J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma and H. Yan, *Nat. Energy*, 2016, **1**, 15027.
- 6 S. Li, L. Ye, W. Zhao, H. Yan, B. Yang, D. Liu, W. Li, H. Ade and J. Hou, *J. Am. Chem. Soc.*, 2018, **140**, 7159.
- 7 Z. Xiao, J. Xue and L. Ding, *Sci. Bull.*, 2017, **62**, 1562.
- 8 S. Zhang, Y. Qin, J. Zhu and J. Hou, *Adv. Mater.*, 2018, **30**, 1800868.
- 9 H. Zhang, H. Yao, J. Hou, J. Zhu, J. Zhang, W. Li, R. Yu, B. Gao, S. Zhang and J. Hou, *Adv. Mater.*, 2018, **30**, 1800613.
- 10 G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323.
- 11 S. Xiao, Q. Zhang and W. You, *Adv. Mater.*, 2017, **29**, 1601391.
- 12 C. McDowell, M. Abdelsamie, M. F. Toney and G. C. Bazan, *Adv. Mater.*, 2018, 1707114.
- 13 Y. Kim, H. R. Yeom, J. Y. Kim and C. Yang, *Energy Environ. Sci.*, 2013, **6**, 1909.
- 14 J. Yuan, Y. Xu, G. Shi, X. Ling, L. Ying, F. Huang, T. H. Lee, H. Y. Woo, J. Y. Kim, Y. Cao and W. Ma, *J. Mater. Chem. A*, 2018, **6**, 10421.
- 15 J. Yuan, M. J. Ford, W. Ma and G. C. Bazan, *J. Mater. Chem. A*, 2017, **5**, 8903.
- 16 Y. Zheng, G. Wang, D. Huang, J. Kong, T. Goh, W. Huang, J. Yu and A. D. Taylor, *Sol. RRL*, 2018, **2**, 1700144.
- 17 H. I. Kim, M. Kim, C. W. Park, H. U. Kim, H.-K. Lee and T. Park, *Chem. Mater.*, 2017, **29**, 6793.
- 18 P. G. Eun, C. Suna, P. S. Yeon, L. D. Hee, C. M. Ju and C. D. Hoon, *Adv. Energy Mater.*, 2017, **7**, 1700566.
- 19 J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, **6**, 497.
- 20 J. S. Moon, C. J. Takacs, S. Cho, R. C. Coffin, H. Kim, G. C. Bazan and A. J. Heeger, *Nano Lett.*, 2010, **10**, 4005.
- 21 J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan and A. J. Heeger, *J. Am. Chem. Soc.*, 2008, **130**, 3619.
- 22 L. Seongyu, K. Jaemin and L. Kwanghee, *Adv. Energy Mater.*, 2016, **6**, 1600970.
- 23 S.-H. Liao, H.-J. Jhuo, Y.-S. Cheng and S.-A. Chen, *Adv. Mater.*, 2013, **25**, 4766.
- 24 Y. Zhao, X. Zhao, Y. Zang, C.-a. Di, Y. Diao and J. Mei, *Macromolecules*, 2015, **48**, 2048.
- 25 A. K. K. Kyaw, D. H. Wang, V. Gupta, W. L. Leong, L. Ke, G. C. Bazan and A. J. Heeger, *ACS Nano*, 2013, **7**, 4569.
- 26 M. Yang, T.-K. Lau, S. Xiao, J. Gao, W. Wang, X. Lu, S. Zhang, J. Wu, C. Zhan and W. You, *ACS Appl. Mater. Interfaces*, 2017, **9**, 35159.
- 27 J. Gao, W. Wang, S. Zhang, S. Xiao, C. Zhan, M. Yang, X. Lu and W. You, *J. Mater. Chem. A*, 2018, **6**, 179.
- 28 D. Gupta, S. Mukhopadhyay and K. S. Narayan, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1309.
- 29 B. Qi and J. Wang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8972–8982.