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ARTICLE

Enhancing the performance of polymer solar cells by tuning the drying process of blend films via changing side chains and using solvent additive

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A series of new conjugated polymers (**P1-P3**) with 3,6-difluorocarbazole as the donor unit and benzooxadiazole as the acceptor unit were synthesized and used as donor materials for polymer solar cells (PSCs). The morphology of blend films was regulated by controlling the drying process via tuning the solubility of polymers and using solvent additive. Enhancing the solubility of polymers via increasing the volume of side chains can decrease the domain size of polymers and using 1,8-diiodooctane (DIO) as a solvent additive can give an even better vertical phase separation, leading to a significant enhancement of power conversion efficiency (PCE) up to 5.71% for **P3** based PSCs. The improving of interface between polymer and PC₇₁BM phases as well as the formation of vertical phase separation after using DIO as an additive are probably responsible for the high open circuit voltage (V_{oc}) of devices.

Introduction

In the last two decades, bulk heterojunction polymer solar cells (BHJ PSCs) with conjugated polymers as the donor and PC₇₁BM as the acceptor have attracted particular attentions because of their advantages of lightweight, low-cost and mechanical flexibility.¹⁻³ Significant progress has been made in recent years and power conversion efficiency (PCE) over 10% has been achieved.⁴⁻⁸ These accomplishments were mostly driven by the design and synthesis of new conjugated polymer materials, the optimization of devices and the investigation of the relationship between the chemical structure of polymers and the photovoltaic performance of devices.

Development of effective methods to tune the morphology of the BHJ layer is a significant task to improve device performance⁹ and the solubility of polymers is very important to afford appropriate phase separation when blending with PC₇₁BM.¹⁰ The morphology of active layer is significantly influenced by the solubility of conjugated polymers. Generally, bad solubility of polymers usually causes oversize domain sizes while evaporating from the solution which goes against the effective dissociation of the exciton. But good solubility, which comes from longer chains, usually affects the stacking of polymers as films. Therefore, using appropriate

side chains to balance the solubility and planarity of conjugated polymers is beneficial to achieve best photovoltaic performance. Active layer with an appropriate vertical phase separation is beneficial to afford high performance of PSCs.¹¹ Conventional devices with a polymer rich bottom surface could enhance the collection of holes by the anode and suppress the bulk and interfacial bimolecular charge recombination. Such vertical phase separation of active layer could be optimized by adding DIO as the additive.¹²

Fluorine has been proved to be a good substituent for acceptor group of donor-acceptor (D-A) alternating polymers, the introduction of F atoms onto acceptor unit could significantly improve the photovoltaic performance of polymers,^{13,14} but the introduction of F atoms onto donor positions may result in a different influence on the photovoltaic performance.^{15,16} Since F atoms exhibit greatly positive effects in the improvement of the photovoltaic performance, extending the study of D-A conjugated polymers with fluorinated donor unit is still of great significance to achieve higher efficiency photovoltaic polymers. Benzooxadiazole (BO) has been proved to be a good acceptor unit for the construction of D-A conjugated polymers used for PSCs.¹⁷ Compared with the commonly used benzothiadiazole (BT) acceptor unit, BO could furnish deeper HOMO level for the resulted polymers. However, due to the high polarity of O atom and the high planarity of BO part, BO based polymers exhibited poor solubility.¹⁸ By changing the side chains of conjugated backbones, **P1**, **P2** and **P3** with fluorinated carbazole as the donor unit, BO as the acceptor unit, and thiophene as the π bridge were synthesized in this

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†Electronic Supplementary Information (ESI) available: Experimental part including TGA curves, SCLC curves, and ¹H NMR spectra of monomers and polymers.

work. All three polymers exhibited worse solubility compared with PC₇₁BM, which would lead to a liquid-solid mechanism in the film drying procedure.¹⁹ But too bad solubility would cause oversized domain sizes in the progress of film drying. By gradually extending the side chains for **P1**, **P2** and **P3**, better solubility and higher hole mobility could be achieved, besides that root-mean-square (RMS) roughness value of the film surface and series resistance values of devices all gradually reduced, which would lead to a higher PCE. XPS experiment demonstrated **P1-3** were all donor rich in the bottom surface, which is beneficial for the hole injection by the electrode. Using DIO as the additive, the fluorescence intensity of polymers was decreased, indicating that the domain size of polymer became smaller. Besides that, hole mobility values of devices were further enhanced, series resistor values of the devices were further reduced, and the RMS roughness values of the active layers were decreased, which demonstrated DIO could optimize the film morphology. X-ray photoelectron spectroscopy (XPS) experiment also demonstrated the contents of **P1-3** in the bottom surface were all enhanced with DIO as the additive, which would lead to better photovoltaic performance. Compared with the non-fluorinated polymer, fluorinated polymers exhibited lower HOMO levels, and open circuit voltage (V_{oc}), short circuit current (J_{sc}) and fill factor (FF) were all improved to achieve higher PCE. Using 2% DIO as the additive, photovoltaic devices based on **P3** showed the best PCE of 5.71%.

Results and discussion

Material Synthesis and Characterization

Scheme 1. Synthesis of monomers and polymers.

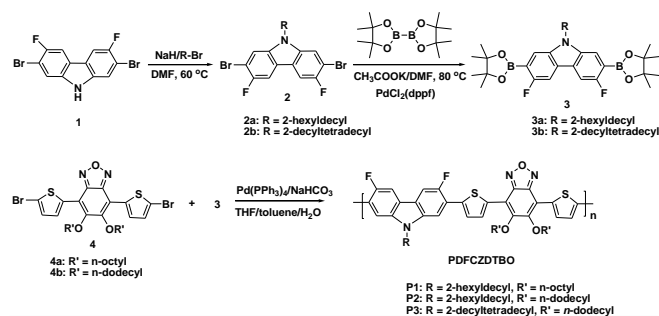
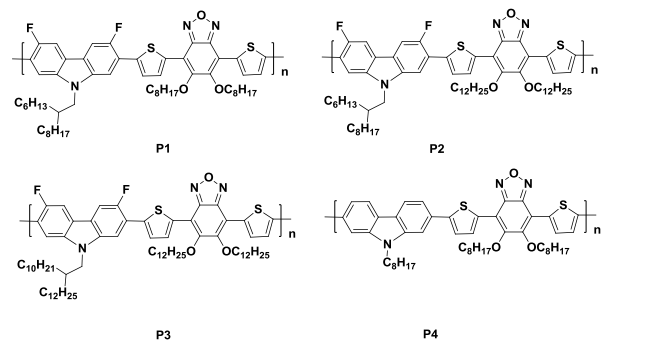


Chart 1



The syntheses of monomers (**3a**, **3b**) and polymers (**P1**, **P2**, and **P3**) are outlined in Scheme 1. 2,7-Dibromo-3,6-difluoro-9H-carbazole(**1**),²⁰ 2,7-dibromo-3,6-difluoro-9-(2-hexyldecyl)-9H-carbazole (**2a**),²⁰ 4,7-bis(5-bromothiophen-2-yl)-5,6-dioctylbenzo[c][1,2,5]oxadiazole (**4a**),²¹ 4,7-bis(5-bromothiophen-2-yl)-5,6-didodecylbenzo[c][1,2,5]oxadiazole (**4b**),²¹ and 3,6-difluoro-9-(2-hexyldecyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**3a**)²⁰ were synthesized according to the literature procedures. **2b** was prepared in a yield of 82% by the reaction of compound **1** and 11-(bromomethyl)tricosane in DMF with NaH as a base. The reaction of **2b** and bis(pinacolato)diboron by Miyaura reaction using PdCl₂(dppf) as the catalyst afforded **3b** in a yield of 62%. Suzuki polycondensation (SPC) of the dibromo monomers (**4a** and **4b**) with diboronic acid ester monomer (**3a**) afforded polymers (**P1** and **P2**) as dark-red solids in yields of 70% and 78%, respectively. SPC of **3b** and **4b** furnished **P3** in a yield of 81% as a dark-red solid. SPCs were carried out in a biphasic mixture of THF/toluene (3:1) and aqueous NaHCO₃ with Pd(PPh₃)₄ as the catalyst precursor. After polymerization, the bromo and boronic acid end-groups were capped by phenylboronic acid and bromobenzene, respectively. The side chains have a great influence on the solubility of polymers and the solubility of polymers can be tuned by changing their side chains. **P1** carrying two octyloxy chains on the 5,6-positions of benzothiadiazole unit and one 2-hexyldecyl chain on the 9-position of 3,6-difluorocarbazole unit exhibited very poor solubility in chloroform (CF), chlorobenzene (CB), 1,2-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene (TCB) at room temperature. Nevertheless, **P1** can be fully dissolved in DCB and TCB at temperature above 115 °C. **P2**, in which the two octyloxy chains on the 5,6-positions of benzothiadiazole unit were changed to two dodecyloxy chains, exhibited slightly better solubility than **P1**. **P2** is also almost insoluble in common organic solvents such as CF, CB, DCB, and TCB at room temperature, but can be fully soluble in CB, DCB, and TCB at temperature above 105 °C. **P3** with replacing the 2-hexyldecyl chain on the 9-position of 3,6-difluorocarbazole unit with 2-decyltetradecyl group showed further improved solubility in comparison with **P2**. **P3** is partially soluble in DCB and TCB at room temperature and can be fully dissolved in CB, DCB, and TCB at temperature above 80 °C. The molecular weights and polydispersity indexes (PDI) of **P1-3** measured by gel permeation chromatography (GPC) at 150 °C using TCB as an eluent and polystyrenes as the calibration standards are summarized in Table 1. Thermal stability of these polymers was investigated with thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10 °C/min. **P1**, **P2**, and **P3** exhibited good thermal stability with 5% weight loss at 327 °C, 323 °C, and 318 °C, respectively, and the results are also summarized in Table 1. No glass transition temperature can be detected for **P1-3** by differential scanning calorimetry (DSC) in the range of 20 to 250 °C at a heating rate 10 °C/min under nitrogen atmosphere. To investigate the packing of polymer chains in the solid state, powdery samples of **P1-3** were investigated by X-ray diffraction (XRD) technique. As shown in Fig 1, **P1** and **P2**

present a relatively intense diffraction peak in the small angle region and a broad peak in the wide angle region, reflecting the lamella stacking and π - π stacking of polymers, respectively. The small angles of 4.51° for **P1** and 3.87° for **P2** revealed that the stacking distances of polymer backbones separated by the flexible side chains are 19.58 \AA for **P1** and 22.81 \AA for **P2**. The diffraction peaks at 20.8° , 20.6° and 20.4° reflex the π - π stacking distances between the polymer backbones, which are calculated to be 4.28 \AA , 4.31 \AA and 4.33 \AA for **P1**, **P2**, and **P3**, respectively. XRD investigations indicated that the π - π packing distance between polymer backbones can be slightly tuned by the side chains.

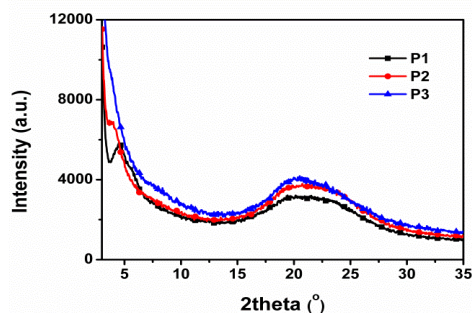


Fig. 1 XRD patterns of **P1-3** powders.

Table 1. M_n , M_w , PDI, and T_d of **P1-3**.

Polymer	M_n (kg/mol) ^a	M_w (kg/mol) ^a	PDI	T_d ($^\circ\text{C}$) ^b
P1	20.1	51.0	2.53	327
P2	22.1	58.1	2.63	323
P3	31.9	77.5	2.43	318

^a M_n , M_w , and PDI were determined by GPC at 150°C with TCB as an eluent calibrated with polystyrene standards.

^b T_d was determined by TGA under N_2 atmosphere based on 5% weight loss.

Optical Properties

UV-vis absorption characteristics of **P1-3** in DCB ($1 \times 10^{-5} \text{ M}$) were investigated at an elevated temperature of 120°C . As shown in Fig. 2a, all polymers exhibit three absorption peaks in the visible region. The peak located at around 386 nm can be attributed to the localized π - π^* transition and the two peaks at long wave length region can be ascribed to the internal charge transfer (ICT) interaction from the carbazole donor unit to the benzooxadiazole acceptor unit. The shoulder peak at about 573 nm can be attributed to the aggregation of polymer chains, and its intensity decreased slightly in the order of **P1**, **P2** and **P3** with the volume of side chains increased gradually. UV-visible absorption spectra of **P1-3** films spin coated on quartz substrates are shown in Fig. 2b. In going from solution to film, the long wave length absorption peak red-shifted from 572 to 582 nm for **P1**, from 573 to 577 nm for **P2**, and from 573 to 574 nm for **P3**. This result indicates that larger side chains can weaken the interaction of polymer in the solid state. The film absorption onsets of **P1-3** are 632 , 625 , and 610 nm , corresponding to optical band gaps ($E_{g, \text{opt}}$) of 1.96 , 2.00 , and 2.03 eV ,

respectively. These data are also summarized in Table 2. In comparison with the non-fluorinated polymer **P4**, the long wave length absorption peaks of **P1** and **P2** became much stronger, indicating that the introduction of F atoms in the donor unit can significantly enhance the interaction of polymers in the solid state. To investigate the influence of DIO as additive on the aggregation of **P1-3** in the blend films, UV-visible absorption spectra of **P1-3**:PC₇₁BM blend films with and without 2% DIO as the additive was also tested. As shown in Fig. S2, all films exhibited a broad absorption in the range from 350 nm to 650 nm . After using 2% DIO as the additive, the intensity of the peaks around 550 nm all significantly decreased, demonstrated using DIO as the additive could reduce the aggregation of **P1-3** in the blend film. To further investigate the influence of DIO as the additive on the charge recombination in the active layer, the fluorescence spectra of blend films also measured. As shown in Fig. S3, after using 2% DIO as the additive, the blend films all exhibited higher fluorescence quenching efficiencies. The enhancement of fluorescence quenching efficiency demonstrated using DIO as the additive could optimize the blend morphology and reduce the charge recombination in the blend films, which would lead to higher V_{oc} of devices.²²⁻²⁷

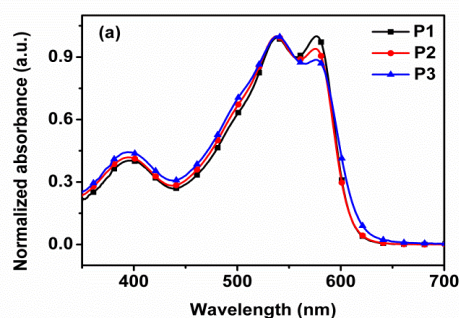
Table 2. Electronic and optical properties of **P1-4**.

Polymer	λ_{max} (nm) solution	λ_{max} (nm) film	$E_{g, \text{opt}}$ (eV) ^a	HOMO (eV)	LUMO (opt, eV) ^b
P1	387, 532, 572	400, 538, 582	1.96	-5.55	-3.59
P2	386, 532, 573	390, 535, 577	2.00	-5.57	-3.57
P3	385, 532, 573	389, 533, 574	2.03	-5.58	-3.55
P4 ^c	-	385, 540	1.93	-5.34	-3.46

^a Calculated from the absorption band edge of polymer film, $E_{g, \text{opt}} = 1240/\lambda_{\text{edge}}$.

^b Calculated by the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g, \text{opt}}$.

^c Reference from literature¹⁹.



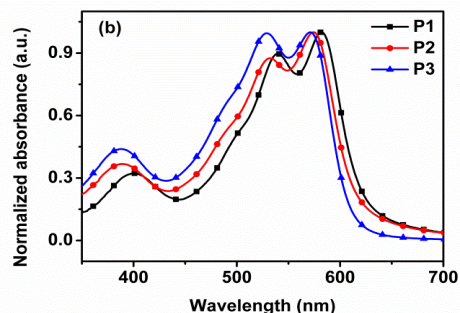


Fig. 2 UV-vis absorption spectra of **P1-3** in DCB solutions at 120 °C (a) and as thin films (b).

Electrochemical properties

Electrochemical properties of **P1-3** films were investigated by cyclic voltammetry on a glassy carbon working electrode. As shown in Fig. 3, the onset oxidation potentials (E_{ox}) of **P1-3** are 0.84, 0.86 and 0.87 eV vs Ag/AgCl reference electrode. HOMO energy levels were determined according to the equation $E_{HOMO} = -e(E_{ox} + 4.71 \text{ eV})$ to be -5.55 eV for **P1**, -5.57 eV for **P2**, and -5.58 eV for **P3**. LUMO levels of **P1**, **P2**, and **P3** were calculated by the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$ to be -3.59, -3.57, and -3.55 eV, respectively. The complete data are summarized in Table 2. The results indicated that increasing the volume of side chains has a subtle influence on electrochemical properties of polymers. Compared with the non-fluorinated **P4**, the presence of two F atoms on the carbazole donor unit lowers the HOMO levels of **P1-3** for about 0.2 eV. The fairly low-lying HOMO levels are beneficial to afford higher V_{oc} for PSCs.

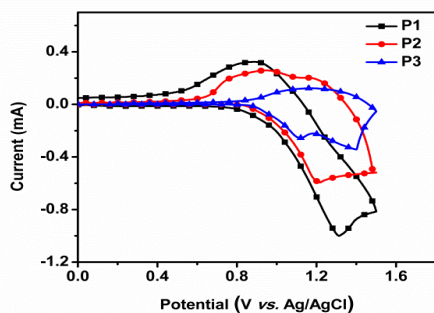
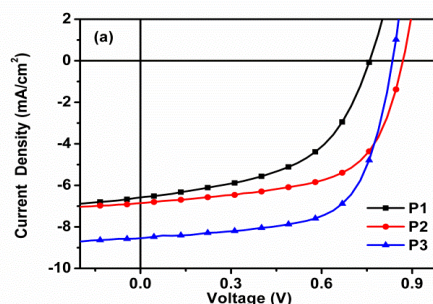


Fig. 3 Cyclic voltammograms of **P1-3** as thin films on a glassy carbon working electrode.

Photovoltaic properties

To investigate the photovoltaic performance of **P1-3** as donor materials, devices with a configuration of ITO/PEDOT:PSS (40 nm)/**P1-3**:PC₇₁BM/LiF (0.5 nm)/Al (100 nm) were fabricated. Detailed studies on the processing solvent, the weight ratio of **P1-3** to PC₇₁BM, the concentration of blend solution, the spin-coating speed, the thickness of active layer, and the amount of 1,8-diiodooctane (DIO) additive were carried out to optimize the device performance. Since the poor solubility of **P1-3** in DCB at room temperature, all devices were fabricated by spin-coating blend solutions at elevated

temperature. For all three polymers, the best plain devices were fabricated with a **P1-3**:PC₇₁BM weight ratio of 1:3.5. Current density-voltage (J - V) curves of the optimized devices are shown in Fig. 4 and the device characteristics are summarized in Table 3. **P1** based devices exhibited a PCE of 2.60 % with a V_{oc} of 0.76 V, a J_{sc} of 6.55 mA/cm², and an FF of 0.52. **P2** based devices demonstrated a PCE of 3.71% with a V_{oc} of 0.89, a J_{sc} of 6.80 mA/cm², and an FF of 0.61. **P3**:PC₇₁BM based devices showed a PCE of 4.69% with a V_{oc} of 0.84 V, a J_{sc} of 8.51 mA/cm², and an FF of 0.65. The results clearly demonstrated that the enhancement of the solubility of polymers can improve the device performance. 1,8-Diiodooctane (DIO) is a good solvent for PC₇₁BM but a poor solvent for conjugated polymers.¹⁹ DIO (2.0% by volume) was therefore used as a processing additive to optimize the device performance, and the results are shown in Table 3. After adding DIO, all devices exhibited improved photovoltaic performance with V_{oc} increased from 0.76 to 0.86 V for **P1**, from 0.89 to 0.93 V for **P2**, and from 0.84 to 0.91 V for **P3**. After adding DIO, the J_{sc} and FF values also slightly increased. The significant enhancement of V_{oc} indicated that the charge recombination in the devices is reduced and enhancement of FF value should be ascribed to the decreasing of series resistance for the devices.^{27,28} To understand why using DIO as an additive can improve the device performance, the morphology of active layers were investigated by atomic force microscopy (AFM), the transport properties of active layers were investigated by the space-charge limited current (SCLC) method, and the element composition of the top and bottom surface of active layers were investigated by XPS (vide infra). These investigations demonstrated that the enhancement of device performance is mainly due to the optimized blend morphology and improvement of vertical phase separation, namely the formation of a polymer rich bottom surface of the active layer, which are beneficial for the reducing of charge recombination and collecting of the charges by the electrode.^{27,29} Our investigations have demonstrated that the use of fluorinated carbazole unit as the donor unit has a positive effect for the photovoltaic performance.



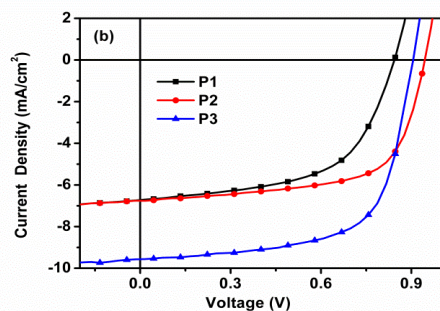


Fig. 4 *J*-*V* curves for P1-3:PC₇₁BM based PSCs without (a) and with 2% DIO as the additive (b).

Table 3. Summary of the photovoltaic properties of P1-4:PC₇₁BM under the illumination of AM 1.5G, 100 mW/cm².

The active layer	DIO	<i>V</i> _{oc} (V)	<i>J</i> _{sc} (mA/cm ²)	<i>FF</i>	PCE (best/average)	Thickness (nm)
P1:PC ₇₁ BM	No	0.76	6.55	0.52	2.60/2.34	98
	2%	0.86	6.76	0.58	3.34/2.90	108
P2:PC ₇₁ BM	No	0.89	6.80	0.61	3.71/3.68	105
	2%	0.93	6.80	0.65	4.12/4.06	115
P3:PC ₇₁ BM	No	0.84	8.51	0.65	4.69/4.63	117
	2%	0.91	9.49	0.66	5.71/5.60	115
P4:PC ₇₁ BM ^a	No	0.85	7.36	0.57	4.20	-

^a Reference from literature¹⁹.

*R*_s is an important factor that determine the *FF* value of photovoltaic devices, it has been demonstrated by many researchers that the reduction of *R*_s usually results in higher *FF*.²⁹ To elucidate what caused the improvement of *FF* value, we measured the *R*_s of devices. As shown in Fig. 5, *R*_s values were calculated from the inverse slope of dark *J*-*V* curves at a voltage of 1.0 V to be 53.25 Ω cm⁻², 21.06 Ω cm⁻² and 10.48 Ω cm⁻² for P1, P2, and P3 based plain devices, respectively. As expected, the reduction of *R*_s resulted in an enhancement of *FF* value. After adding DIO, the *R*_s values for P1, P2, and P3 based devices were decreased to 46.91 Ω cm⁻², 14.59 Ω cm⁻², and 5.40 Ω cm⁻², respectively, which are consistent with the increasing of *FF* obtained from *J*-*V* measurement. This reducing could be ascribed to the optimized morphology by extending the side chain and using DIO as the additive (vide infra). These data are summarized in Table 4.

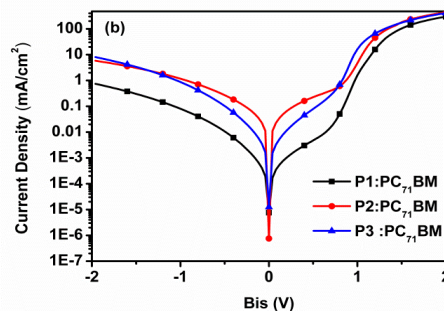
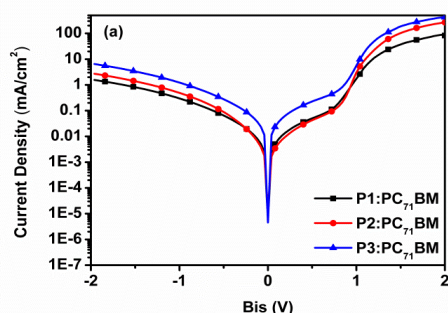


Fig. 5 Series resistor of devices based on P1-3:PC₇₁BM as cast (a) and with 2% DIO as the additive (b).

To examine the veracity of *J*_{sc}, external quantum efficiencies (EQEs) of devices fabricated without and with 2.0% DIO were measured. As shown in Fig. 6, all devices showed a broad EQE response from 350 to 700 nm. For plain devices, the EQE maximum reached 31% at 500 nm for P1, 44% at 542 nm for P2, and 53% at 467 nm for P3. With increasing the volume of side chains, namely the solubility of polymers, the EQE value increased. After adding 2.0% DIO as the additive, for three polymers EQE values only slightly increased. The integration of EQE curves afforded similar *J*_{sc} values to the *J*-*V* measurement, indicating that the *J*_{sc} values obtained from *J*-*V* measurement are reliable.

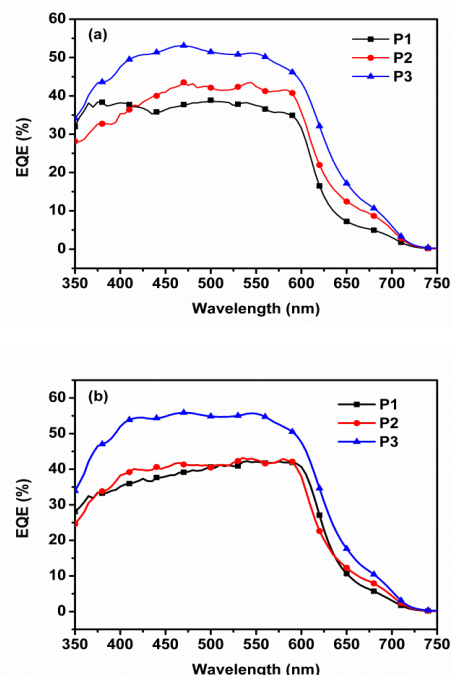


Fig. 6 EQE of P1-3:PC₇₁BM based devices as cast (a) and with 2% DIO as the additive (b).

Transport Properties.

High efficiency PSCs require that the active layers are of balanced electron and hole mobility. Higher hole mobility is beneficial for achieving higher J_{sc} and FF . Hole mobilities (μ_h) of **P1-3**:PC₇₁BM (1:3.5) blend films were measured by the space-charge limited current (SCLC) method. Hole-only devices with a structure of ITO/PEDOT:PSS (30 nm)/**P1-3**:PC₇₁BM/Au (100 nm) were fabricated. Dark $J-V$ curves were fitted by using the Mott–Gurney equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where J is the space charge limited current, ϵ_0 is the vacuum permittivity, ϵ_r is the permittivity of the active layer, μ is the hole mobility, and L is the thickness of the active layer. As shown in Fig. S4, μ_h values of **P1**:PC₇₁BM, **P2**:PC₇₁BM, and **P3**:PC₇₁BM based plain devices were calculated to be 1.1×10^{-6} , 3.3×10^{-5} , and 9.3×10^{-5} cm² V⁻¹ s⁻¹ respectively. The enhancement of hole mobility with increasing the volume of side chains should be ascribed to the better film morphology and lower R_s (vide supra). After adding 2.0% DIO, μ_h values of **P1**, **P2** and **P3** based devices were enhanced to 1.6×10^{-5} , 3.4×10^{-5} , and 1.1×10^{-4} cm² V⁻¹ s⁻¹, respectively.

XPS measurement

The vertical distribution of the donor and acceptor materials in the active layer is very crucial for the performance of devices. Elemental compositions of the top (close to LiF layer) and bottom (close to PEDOT:PSS layer) surfaces of the active layer in a depth of few nanometers were therefore investigated by XPS. The top surface XPS experiment was conducted with the blend film on a glass substrate, and the bottom surface XPS experiment was conducted with a blend film which was spin-coated onto PEDOT:PSS surface, floated on the surface of pure water surface, and transferred onto a silicon substrate with the buried surface upward. The element compositions of sulfur (S) and carbon (C) at the top and bottom surfaces are summarized in Table 4. Because XPS is not a quantitative analysis method, these data could be used for semi-quantitative analysis of the distribution of two components.^{12, 30} XPS results showed that the content of S element at the bottom surface is much higher than that at the top surface, indicating that the blend films are of a vertical phase separation with a PC₇₁BM-rich top surface and a polymer-rich bottom surface. Such a vertical phase separation is beneficial to achieve high performance for conventional polymer solar cells. The formation of vertical phase separation is probably due to the following reasons. The polymers exhibit poorer solubility in DCB than PC₇₁BM and they are prone to precipitate before the liquid-liquid phase separation occurs. Due to the centrifugation effect during spin-coating, the polymer precipitated could probably submerge to the bottom, the PC₇₁BM-rich DCB solution could be at the surface of the active layer, and finally the drying of the blend film leads to a vertical phase separation with a PC₇₁BM-rich top surface and a polymer-rich bottom surface. Since DIO is a good solvent for PC₇₁BM and a poor solvent for the polymers, the use 2.0% DIO as the additive will further promote the process of precipitation and retard the drying process of films.¹² As confirmed by the XPS results, the contents of S element further increased, which are close to

that of pure polymers after using 2.0% DIO as the additive. Compared with the corresponding active layers spin coated without using DIO, the polymer content at the top surface also slightly increased after the addition of DIO, similar to the literature results.¹² The reason for that is unclear at present time. Increasing the ohmic contact between the active layer and the electrode could be beneficial for the reducing of R_s and induce lower charge combination, which could lead to higher V_{oc} .³¹⁻³³ Such a vertical phase separation with almost a pure polymer thin layer at the bottom surface of the active layer was also beneficial for lowering the R_s and reducing the charge recombination at the bottom surface of the active layer.³⁴

Table 4. XPS surface element composition and series resistor of devices based on **P1-3**:PC₇₁BM.

Devices	DIO	Top		Bottom		R_s (Ω cm ⁻²)
		S (%)	C (%)	S (%)	C (%)	
P1 :PC ₇₁ BM	No	2.06	88.51	6.43	66.09	53.25
	2%	2.22	88.44	6.50	65.37	46.91
P2 :PC ₇₁ BM	No	1.47	90.02	5.98	67.89	21.06
	2%	2.06	88.51	6.04	67.76	14.59
P3 :PC ₇₁ BM	No	1.17	91.14	5.48	67.97	10.48
	2%	1.32	90.55	5.64	67.77	5.40

Film morphology

Film morphology of **P1-3**:PC₇₁BM blend films spin coated from DCB solutions without and with 2% DIO as the processing additive is investigated by AFM in the tapping mode. As shown in Fig. 7, the **P1**:PC₇₁BM films spin coated from DCB solution exhibited a rather rough surface with a root-mean-square (RMS) roughness value of 14.5 nm. With increasing the volume of flexible side chains, RMS values of **P2** and **P3** based blend films spin coated from DCB solutions were reduced to 7.24 nm and 3.41 nm, respectively. As indicated before, the solubility of **P2** and **P3** is gradually improved with the presence of elongated flexible side chains. The solubility of **P1-3** in DCB is poorer than that of PC₇₁BM. Therefore, we predict that the polymers can precipitate first in solutions after spin-coating the hot blending solution onto the cold substrate before the film drying. The film drying procedure could be a liquid-solid mechanism. Due to the extremely poor solubility of **P1** in DCB at room temperature, **P1** is prone to form rough film morphology due to the solid-liquid phase separation¹⁷. **P3** exhibited the best solubility among these three polymers, as observed by AFM experiments, the film morphology of **P3** based active layer is more uniform. **P2** exhibits medium solubility, and the domain size formed by **P2** is also of the medium size. After adding 2% DIO as the additive, the RMS roughness values of **P1-3** based blend films were slightly decreased, which demonstrated DIO could optimize the film morphology. Smother morphology usually indicates phase separation in smaller scale, which would be beneficial for the reducing of charge recombination.³⁵ The relatively low V_{oc} of **P1** based devices could be ascribed to the charge recombination caused by big domain sizes in the blend

films. The RMS roughness values of **P1-3** based devices all decreased after 2% DIO adding into the active layer, demonstrated that DIO could optimized the morphology of devices and afford more donor-acceptor interface, which would be beneficial to reduce the charge recombination and lead to higher V_{oc} .³⁶ Due to the domain size formed by liquid-solid phase separation became smaller, **P3**:PC₇₁BM based PSCs gave the highest power conversion efficiency of 5.71% among these three polymers.

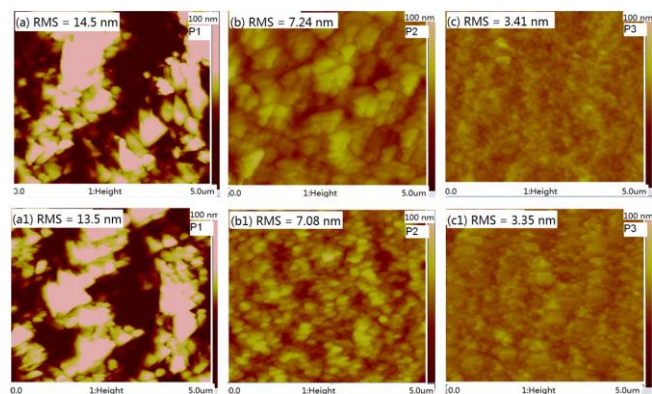


Fig. 7 AFM height images ($5 \mu\text{m} \times 5 \mu\text{m}$) of **P1-3**:PC₇₁BM blend films spin-coated from DCB solutions without (a-c) and with 2.0% DIO (a1-c1).

Conclusions

In summary, a series of new conjugated polymers (**P1-P3**) with 3,6-difluorocarbazole as the donor unit and benzooxadiazole as the acceptor unit were synthesized and used as donor materials for PSCs. These polymers exhibited poorer solubility than PC₇₁BM in DCB. Among them, **P1** exhibited the poorest solubility, leading to the formation of large polymer domains due to the liquid-solid phase separation in the drying of blend films. By gradually extending the side chains for **P2** and **P3**, the solubility of polymers was increased, and the root mean square (rms) roughness values of blend films and the domain size of polymers decreased. Meanwhile, the hole mobility and series resistance value were increased and decreased, respectively, which were beneficial to achieve higher PCE. For all polymers, using DIO as the solvent additive, series resistance values of devices were further reduced and hole mobility were slightly increased. XPS experiments also demonstrated for all polymers that the bottom surface of active layers processed with DIO as the additive became more polymer-rich, which is beneficial for the hole injection to the electrode. Using DIO also could optimize the film morphology and induce better mix property, lower R_s value, and higher fluorescence quenching efficiency, which would be beneficial for the reducing of charge combination, leading to higher V_{oc} . After optimization, PSCs based on **P3** finally gave the best PCE of 5.71%. Compared with the non-fluorinated polymer, fluorinated polymers exhibited lower HOMO levels. V_{oc} , J_{sc} and FF were all improved to furnish higher PCE. These preliminary results also demonstrated that the introduction of fluorine atoms at donor unit is an effective way to achieve higher PCE.

Experimental Part

2,7-dibromo-9-(2-decyltetradecyl)-3,6-difluoro-9H-carbazole (2b). A mixture of compound **1** (3.61 g, 10.0 mmol), NaH (60% in oil) (0.60 g, 15.0 mmol), 11-(bromomethyl)tricosane (5.01 g, 12.0 mmol) and DMF (50 mL) was stirred at 60 °C overnight under nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was partitioned between water (200 mL) and dichloromethane (DCM, 50 mL). The organic layer was separated; the aqueous layer was extracted with DCM (50 mL \times 3); and the combined organic layers were washed with brine (50 mL \times 3), dried over anhydrous MgSO₄, and evaporated to dryness. The residue was further purified by chromatography on silica gel with petroleum ether as an eluent to yield **2b** (5.72 g, 82%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.71-7.73 (d, J = 8.4 Hz, 2H), 7.51-7.52 (d, J = 5.6 Hz, 2H), 4.04-4.06 (d, J = 7.6 Hz, 2H), 2.05 (s 1H), 0.86-1.25 (m, 47H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 141.81, 122.48, 121.38, 121.21, 119.63, 112.29, 47.83, 37.56, 35.49, 33.27, 31.92, 31.86, 31.77, 31.65, 29.89, 29.58, 29.49, 29.26, 28.72, 28.01, 26.37, 26.35, 22.66, 22.63, 15.22, 14.12, 14.09. MALDI-TOF (m/z): M^+ calculated for C₃₆H₅₃Br₂F₂N, 697.62; found: 697.58.

9-(2-decyltetradecyl)-3,6-difluoro-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (3b). A mixture of compound **2b** (1.00 mmol), bis(pinacolato)diboron (0.61 g, 2.40 mmol), KOAc (0.30 g, 5.00 mmol), PdCl₂(dppf) (0.22 mg, 0.03 mmol), and DMF (10 mL) was stirred at 80 °C for 3 d under nitrogen atmosphere. After cooling down to room temperature, water (200 mL) was added, the mixture was extracted with ethyl acetate (50 mL \times 3), and the combined organic layers were washed with brine (50 mL \times 3), dried over anhydrous MgSO₄, and evaporated to dryness. The residue was purified by chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1, v/v) to yield **3b** (0.49 g, 62%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.21-8.22 (d, J = 4.0 Hz, 2H), 7.62-7.64 (d, J = 8.8 Hz, 2H), 3.88-3.90 (d, J = 7.6 Hz, 2H), 2.21 (s, 1H), 1.01-1.41 (m, 71H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 140.90, 125.00, 124.69, 119.90, 115.66, 111.71, 47.33, 37.66, 35.59, 33.29, 32.10, 31.89, 31.80, 31.67, 31.63, 29.92, 29.57, 29.53, 29.27, 28.55, 27.88, 26.52, 26.39, 26.32, 24.92, 22.67, 22.59, 15.44, 14.89, 14.11, 13.97. MALDI-TOF (m/z): M^+ calculated for C₄₈H₇₇B₂F₂NO₄, 791.75; found: 791.70.

General procedure for the preparation of P1-3. A mixture of **3** (0.30 mmol), compound **4** (0.30 mmol), NaHCO₃ (1.25 g, 9 mmol), THF (20 mL), toluene (7 mL), and H₂O (2 mL) was degassed before and after Pd(PPh₃)₄ (6.9 mg, 5.96 μ mol) was added. The mixture was heated to reflux and stirred for 3 d under N₂ atmosphere. Phenylboronic acid (10 mg) and bromobenzene (0.2 mL) were added successively at a time interval of 12 h to end-cap the bromo and boronic acid endgroups, respectively. After cooling down to room temperature, water (100 mL) and chloroform (100 mL) were added. The organic layer was separated, washed with water (50 mL \times 3), and concentrated by evaporation of most of the solvent. The residue was poured into a large amount of acetone, and the resulting precipitates were collected by filtration and washed with acetone. The crude product was dissolved in a large amount of hot chlorobenzene and

filtrated. After the removal of most of the solvent, the resulted concentrated solution was precipitated into a large amount of acetone and the precipitates were collected by filtration and dried under vacuum.

P1. **3a** and **4a** were used to synthesize **P1** according to the procedure described above. **P1** was obtained as a dark-red solid (196 mg, 70%). $^1\text{H NMR}$ (400 MHz, 1,2-dichlorobenzene- d_4): δ (ppm) 8.92-9.08 (m, 2H), 7.94-8.00 (m, 6H), 4.45-4.51 (m, 6H), 1.03-2.40 (m, 62H). GPC (PS standards): $M_w = 51.0 \text{ kg mol}^{-1}$, $M_n = 20.1 \text{ kg mol}^{-1}$, and PDI = 2.53.

P2. **3a** and **4b** were used to synthesize **P2** according to the above described procedure. **P2** was obtained as a dark-red solid (245 mg, 78%). $^1\text{H NMR}$ (400 MHz, 1,2-dichlorobenzene- d_4): δ (ppm) 9.08 (m, 2H), 7.95-8.01 (m, 6H), 4.44-4.53 (m, 6H), 1.06-2.45 (m, 78H). GPC (PS standards): $M_w = 58.1 \text{ kg mol}^{-1}$, $M_n = 22.1 \text{ kg mol}^{-1}$, and PDI = 2.63.

P3. **3b** and **4b** were used to synthesize **P3** according to the procedure described above. **P3** was obtained as a dark-red solid (282 mg, 81%). $^1\text{H NMR}$ (400 MHz, 1,2-dichlorobenzene- d_4): δ (ppm) 8.78-8.94 (m, 2H), 7.80-7.86 (m, 6H), 4.31-4.37 (m, 6H), 0.89-2.26 (m, 94H). GPC (PS standards): $M_w = 77.5 \text{ kg mol}^{-1}$, $M_n = 31.9 \text{ kg mol}^{-1}$, and PDI = 2.43.

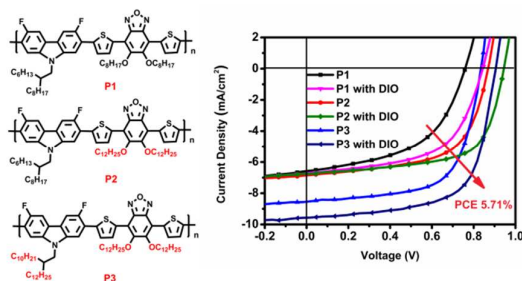
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References

- 1 Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135.
- 2 Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photon.*, 2012, **6**, 591.
- 3 X. Zhan and D. Zhu, *Polym. Chem.*, 2010, **1**, 409.
- 4 Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell and Y. Cao, *Nat. Photonics*, 2015, **9**, 174.
- 5 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat. communications*, 2014, **5**, 5293.
- 6 S. H. Liao, H. J. Jhuo, P. N. Yeh, Y. S. Cheng, Y. L. Li, Y. H. Lee, S. Sharma and S. A. Chen, *Sci. Rep.*, 2014, **4**, 6813.
- 7 C. Liu, C. Yi, K. Wang, Y. Yang, R. S. Bhatta, M. Tsige, S. Xiao and X. Gong, *ACS Appl. Mater. Inter.*, 2015, **7**, 4928.
- 8 S. Liu, P. You, J. Li, J. Li, C. S. Lee, B. S. Ong, C. Surya and Y. Feng, *Energ. Environ. Sci.*, 2015, **8**, 1463.
- 9 H. L. Yip and A. K. Y. Jen, *Energ. Environ. Sci.*, 2012, **5**, 5994.
- 10 J. J. van Franeker, M. Turbiez, W. Li, M. M. Wienk and R. A. J. Janssen, *Nat. Commun.*, 2015, **6**, 6229.
- 11 X. Guo, N. Zhou, S. J. Lou, J. Smith, D. B. Tice, J. W. Hennek, R. Ponce Ortiz, J. T. Lopez Navarrete, S. Li, J. Strzalka, L. X. Chen, R. P. H. Chang, A. Facchetti and T. J. Marks, *Nat. Photon.*, 2013, **7**, 825.
- 12 Z. Lu, B. Jiang, X. Zhang, A. Tang, L. Chen, C. Zhan and J. Yao, *Chem. Mater.*, 2014, **26**, 2907.
- 13 H. Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photon.*, 2009, **3**, 649.
- 14 H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem. Int. Edit.*, 2011, **50**, 2995.
- 15 Y. Liang, D. Feng, Y. Wu, S. T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792.
- 16 M. Zhang, X. Guo, S. Zhang and J. Hou, *Adv. Mater.*, 2014, **26**, 1118.
- 17 S. Shi, X. Xie, P. Jiang, S. Chen, L. Wang, M. Wang, H. Wang, X. Li, G. Yu and Y. Li, *Macromolecules*, 2013, **46**, 3358.
- 18 H. Chen, J. Peet, S. Hu, J. Azoulay, G. Bazan and M. Dadmun, *Adv. Funct. Mater.*, 2014, **24**, 140.
- 19 S. Kouijzer, J. J. Michels, M. van den Berg, V. S. Gevaerts, M. Turbiez, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2013, **135**, 12057.
- 20 H. Wei, Y. H. Chao, C. Kang, C. Li, H. Lu, X. Gong, H. Dong, W. Hu, C. S. Hsu and Z. Bo, *Macromol. Rapid Comm.*, 2015, **36**, 84.
- 21 B. Zhang, X. Hu, M. Wang, H. Xiao, X. Gong, W. Yang and Y. Cao, *New J. Chem.*, 2012, **36**, 2042.
- 22 J. Liu, Y. Shi and Y. Yang, *Adv. Funct. Mater.*, 2001, **11**, 420.
- 23 C. Ramsdale, J. Barker, A. Arias, J. MacKenzie, R. Friend and N. Greenham, *J. Appl. Phys.*, 2002, **92**, 4266.
- 24 J. Kim, J. S. Yeo, H. G. Jeong, J. M. Yun, Y. A. Kim and D. Y. Kim, *Sol. Energ. Mat. Sol. C*, 2014, **125**, 253.
- 25 S. Yamamoto, A. Orimo, H. Ohkita, H. Benten and S. Ito, *Adv. Energ. Mater.*, 2012, **2**, 229.
- 26 M. D. Perez, C. Borek, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2009, **131**, 9281.
- 27 K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs and J. V. Manca, *Nat. Mater.*, 2009, **8**, 904.
- 28 B. Qi and J. Wang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8972.
- 29 Q. Yang, J. Wang, X. Zhang, J. Zhang, Y. Fu and Z. Xie, *Sci. China Chem.*, 2015, **2**, 309.
- 30 C. Bruner, F. Novoa, S. Dupont and R. Dauskardt, *ACS Appl. Mater. Inter.*, 2014, **6**, 21474.
- 31 Z. A. Page, Y. Liu, V. V. Duzhko, T. P. Russell and T. Emrick, *Science*, 2014, **346**, 441.
- 32 V. Mihailetschi, P. Blom, J. Hummelen and M. Rispens, *J. Appl. Phys.*, 2003, **94**, 6849.
- 33 C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374.
- 34 W. C. Tsoi, S. J. Spencer, L. Yang, A. M. Ballantyne, P. G. Nicholson, A. Turnbull, A. G. Shard, C. E. Murphy, D. D. Bradley and J. Nelson, *Macromolecules*, 2011, **44**, 2944.
- 35 A. Gadisa, M. Svensson, M. R. Andersson and O. Inganäs, *Appl. Phys. Lett.*, 2004, **84**, 1609.
- 36 K. Vandewal, A. Gadisa, W. D. Oosterbaan, S. Bertho, F. Banishoeib, I. Van Severen, L. Lutsen, T. J. Cleij, D. Vanderzande and J. V. Manca, *Adv. Funct. Mater.*, 2008, **18**, 2064.

Graphical abstract



The PCE of 5.71% for PSCs has been achieved by tuning the drying process of blend films via adjusting side chains and using DIO additives