# Effect of the alkyl chain length of $C_{70}$ -PCBX acceptors on the device performance of P3HT : $C_{70}$ -PCBX polymer solar cells<sup>†</sup>

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A series of soluble  $C_{70}$ -derivatives ( $C_{70}$ -PCBX) was synthesized by varying the alkyl chain length of the adduct (X = R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub>, R<sub>7</sub>, R<sub>9</sub>) attached to the  $C_{70}$ -polyhedron. After blending with P3HT, bulk heterojunction polymer solar cells were fabricated, and their performances were evaluated. As the alkyl chain length increased, phase segregation between the P3HT and  $C_{70}$ -PCBX domains in the P3HT :  $C_{70}$ -PCBX blend active layer increased, which enhanced the device performance to a moderate degree. The performance enhancement may have been due to the increased solubility and self-aggregation of  $C_{70}$ -PCBX as a result of the longer alkyl chains, as was predicted by molecular simulations. The nanomorphologies of the P3HT :  $C_{70}$ -PCBX active layers offered an explanation for the trend in solar cell performance: as the series progressed from  $C_{70}$ -PCBR<sub>1</sub> to  $C_{70}$ -PCBR<sub>7</sub>, the open circuit voltage and the short circuit current gradually increased, followed by a slight drop for  $C_{70}$ -PCBR<sub>9</sub>. An optimal overall power conversion efficiency was observed for  $C_{70}$ -PCBR<sub>7</sub> with a P3HT :  $C_{70}$ -PCBR<sub>7</sub> blend ratio of 1 : 0.8 to 1 : 0.9.

# Introduction

In addition to the known advantages of organic solar cells, which include low manufacturing costs, light weight, thinness, flexibility and possible transparency, solution-based polymer solar cells provide manufacturing flexibility; for example, such solar cells can be fabricated using ink-jet, spray, brush, doctor blading, or roll-to-roll printing technologies.<sup>1</sup> A dramatic increase in the energy conversion efficiencies of solution-based polymer solar cells may be achieved by the introduction of soluble fullerene derivatives,<sup>2</sup> and the success of this method subsequently attracted the interest of the solar industry. Recently, the energy conversion efficiency for a mixture of poly-3-hexylthiophene (P3HT) and phenyl-C61-butyric acid methyl ester (C<sub>60</sub>-PCBM) reached nearly 5%.<sup>3</sup>

The C<sub>70</sub> analog (C<sub>70</sub>-PCBM) of C<sub>60</sub>-PCBM is a key material that provides an appropriate match for low band gap polymers. Because many low band gap polymers do not have high absorption coefficients at short wavelengths, the strong absorption of visible light due to the asymmetric structure (contrasting with the symmetric C<sub>60</sub>) makes C<sub>70</sub>-derivatives good counterparts for low band gap polymers. By virtue of the introduction of the C<sub>70</sub>-PCBM counterpart, many recently developed low band gap polymers have broken the energy conversion efficiency record and reached efficiencies of nearly 7%.<sup>4</sup>

Following the success of  $C_{60}$ - and  $C_{70}$ -PCBMs, many new soluble  $C_{60}$ -,  $C_{70}$ - and other derivatives have been synthesized,

although most have not shown properties superior to those of  $C_{60}$ - and  $C_{70}$ -PCBM.<sup>5,6</sup> Only a few novel materials, such as endohedral or bis-indene fullerenes, have shown good photovoltaic properties.<sup>7</sup> The search has continued for new types of electron acceptor materials, such as perylene and graphene,<sup>8</sup> for use in solution-based organic solar cells. However, new materials that perform better than fullerene derivatives have not yet been identified.

In bulk-heterojunction polymer solar cells, securing percolation pathways for hole and electron transfer is a key issue. Two different approaches can be taken, depending on the properties of the donor polymers. In crystalline polymers, particularly in the case of regioregular P3HT, the optimal domain size of the polymer and fullerene derivatives, in terms of charge percolation, is achieved through thermal9 or solvent annealing.10 Most of the recently developed high-efficiency low band gap polymers have been amorphous, and these amorphous polymers cannot be optimized through thermal or solvent annealing. In the case of these amorphous polymers, a small quantity of high boiling point ingredients is added to the active material blend solution as the only effective method for improving the percolation pathways via selective solvation of the fullerene derivatives.<sup>11,12</sup> Unfortunately, the high boiling additive must be removed prior to packaging the device because it may negatively impact performance during long-term operation. More reliable methods for controlling the nanomorphology of the active layers are required in order to successfully establish bulk-heterojunction organic solar cells.

In this work, we introduced alkyl groups with various lengths to the terminal ester of  $C_{70}$ -PCBX ([6,6]-phenyl C71-butyric acid alkyl ester). This region was anticipated to directly interact with neighboring molecules. We investigated the physico-chemical and photovoltaic properties of the blend using the P3HT polymer as a donor.

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## Experimental

## Materials

Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl  $C_{71}$ -butyric acid methyl ester ( $C_{70}$ -PCBR<sub>1</sub>) were purchased from Rieke Metal Ltd. and Nano-C, respectively, and were used without further treatment.

The  $C_{70}$ -PCBR<sub>3</sub>-R<sub>9</sub> were synthesized *via* UV irradiation of [5,6]-isomers in an ODCB solution, which were prepared by a modified procedure described in the literature (Scheme 1).<sup>13,14</sup>

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained with a Bruker DPX-300 instrument as indicated, at 298 K using TMS as an internal standard. MALDI-TOF data was acquired on a Voyager-DE STR instrument in Reflector Mode with a laser intensity of 2000. 200 shots were averaged to give the resulting spectra.

#### Synthesis

General procedure for the synthesis of [6,6]-phenyl  $C_{71}$ -butyric acid alkyl esters (**3a–3d**).

[6,6]-Phenyl C<sub>71</sub>-butyric acid propyl ester 3a. A mixture of propyl 5-phenyl-5-(2-tosylhydrazono)pentanoate 2a (0.89 g, 2.22 mmol) and sodium methoxide (0.12 g, 2.20 mmol) were suspended in dry pyridine (30 mL) under an atmosphere of dry nitrogen and the mixture was stirred at RT for 30 min. To the mixture a solution of C<sub>70</sub> (1.7 g, 2.00 mmol) in ODCB (75 mL) was added. The resulting mixture was heated to 75-90 °C and allowed to react for 12 h in the dark under an atmosphere of  $N_2$ . After cooling down to RT the reaction mixture was irradiated with a 400 W sodium lamp for 2 h. The volatile components were evaporated in vacuo. The crude product was purified using column chromatography (Silica gel/ODCB). After elution of the recovered C70, the fraction containing mono-adduct [70] PCBM isomers was collected. The solvent was removed in vacuo and the remaining solid was transferred to a centrifugal bottle using a minimal amount of toluene and subsequently precipitated with MeOH. The residue was washed with MeOH (2x) and dried in

*vacuo* at 70 °C for 12 h. Yield: 1.4 g (65%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz);  $\delta$  (ppm): 7.92–7.88 (m, 2H), 7.55–7.42 (m, 3H), 4.04–4.00 (m, 2H), 2.51–2.41 (m, 4H), 2.21–2.12 (m, 2H), 1.70–1.61 (m, 2H), 0.95–0.89 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz);  $\delta$  (ppm): 173.1, 126.4–155.9, 71.8, 69.7, 66.2, 35.9, 34.1, 34.0, 22.0, 21.7, 10.5. MALDI-TOF: M<sup>+</sup> = 1059 *m*/*z* (calcd. 1058.1 g mol<sup>-1</sup>).

**[6,6]-Phenyl C**<sub>71</sub>-butyric acid pentyl ester 3b. Yield: 1.3 g (62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz);  $\delta$  (ppm): 7.90–7.77 (m, 2H), 7.55–7.41 (m, 3H), 4.12–4.04 (m, 2H), 2.48–2.41 (m, 4H), 2.19–2.07 (m, 2H), 1.62–1.60 (m, 2H), 1.32–1.25 (m, 4H), 0.94–0.89 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz);  $\delta$  (ppm): 173.1, 128.2–155.9, 71.8, 69.7, 64.8, 35.9, 34.1, 34.0, 28.3, 28.1, 22.3, 21.7, 14.0. MALDI-TOF: M<sup>+</sup> = 1087 *m*/*z* (calcd. 1086.4 g mol<sup>-1</sup>).

[6,6]-Phenyl C<sub>71</sub>-butyric acid heptyl ester 3c. Yield: 1.3 g (61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz);  $\delta$  (ppm): 7.92–7.89 (m, 2H), 7.55–7.43 (m, 3H), 4.03 (m, 2H), 2.51–2.42 (m, 4H), 2.35–2.21 (m, 2H), 1.67–1.65 (m, 2H), 1.35–1.22 (m, 8H), 0.90–0.84 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz);  $\delta$  (ppm): 173.1, 128.2–155.9, 71.8, 69.7, 64.8, 35.9, 34.1, 34.0, 31.7, 28.9, 28.6, 25.9, 22.6, 21.7, 14.1. MALDI-TOF: M<sup>+</sup> = 1116 *m*/*z* (calcd. 1114.4 g mol<sup>-1</sup>).

**[6,6]-Phenyl C**<sub>71</sub>-butyric acid nonyl ester 3d. Yield: 1.2 g (55%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz);  $\delta$  (ppm): 7.90–7.77 (m, 2H), 7.53–7.41 (m, 3H), 4.12–4.05 (m, 2H), 2.48–2.42 (m, 4H), 2.18–2.05 (m, 2H), 1.61–1.59 (m, 2H), 1.30–1.23 (m, 12H), 0.91–0.85 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz);  $\delta$  (ppm): 173.1, 128.5–155.9, 71.8, 69.7, 64.8, 35.8, 34.1, 34.0, 31.8, 29.5, 29.2, 28.6, 25.9, 22.6, 21.7, 14.1. MALDI-TOF: M<sup>+</sup> = 1143 *m/z* (calcd. 1142.5 g mol<sup>-1</sup>).

#### Photovoltaic device fabrication

For the fabrication of active layers composed of poly(3-hexylthiophene) (P3HT) and [6,6]- phenyl C71-butyric acid alkyl ester (C<sub>70</sub>-PCBX), blend solutions with weight ratios of 1: 0.7-1: 1P3HT: C<sub>70</sub>-PCBX were prepared using chlorobenzene as



a solvent. The solutions were stirred overnight and spun-cast onto a quartz plate to measure the optical absorption and photoluminescence (PL) spectral properties.

The polymer solar cells were fabricated using a typical sandwich structure of ITO/PEDOT:PSS/active layer/LiF/Al. The ITO coated glass substrates were cleaned by a routine cleaning procedure that included sonication in detergent, distilled water, acetone, and 2-propanol. The PEDOT:PSS (Clevios P. H. C. Starck) layer with thickness of 50 nm was spin-coated onto a cleaned ITO substrate after exposing the ITO surface to ozone for 10 min to improve the wetting properties of the PEDOT:PSS. The PEDOT:PSS layer was then baked on a hotplate at 140 °C for 10 min and transported to a glovebox with an argon atmosphere. Again, the blend solution of P3HT and C70-PCBX in chlorobenzene (weight ratios of 1: 0.7-1: 1) was spin-coated on top of the PEDOT:PSS layer to constitute the active layer. The thickness of the active layer was fixed at 90 nm by varying the spin speed, as measured using a profilometer with an accuracy of 1 nm (KLA Tencor Alpha-step IQ). The device structure was completed by thermally depositing the cathode electrode consisting of LiF (0.6 nm) and Al (110 nm) onto the photoactive layer through a shadow mask with an aperture size of 9 mm<sup>2</sup> under  $3 \times 10^{-6}$  Torr vacuum. Finally, fabricated devices were annealed at 150 °C for 30 min to improve the morphology of the active layer and the performance of the devices.

#### Characterization

Current density–voltage (J–V) characteristics of all polymer solar cells were measured under the illumination of simulated solar light with 100 mW cm<sup>-2</sup> (AM 1.5 G) using an Oriel 1000 W solar simulator. Electric data were recorded using a Keithley 236 source-measure unit, and all characterizations were carried out in an ambient environment. The illumination intensity used was confirmed by a standard KG5 filtered Si photovoltaic cell from PV Measurements Inc., which was calibrated at the National Renewable Energy Laboratory (NREL).

The incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 360 to 800 nm (PV Measurements Inc.) using a halogen lamp as a light source. The light intensity at each wavelength was calibrated using a reference silicon photodiode.

The work function measurement of C70-PCBXs was conducted with a UV intensity of 10 nW on a low-energy photoelectron spectrometer (Riken-Keiki, AC-2). The samples were prepared by spin-coating a 0.2 wt% C70-PCBX solution dissolved in chlorobenzene onto pre-cleaned glass substrates at 400 rpm in a glove box. The surface morphology of  $P3HT : C_{70}-PCBX =$ 1:0.9 films was imaged by AFM (DI3100, Veeco) operating in tapping mode. X-ray diffraction (XRD) patterns of  $P3HT : C_{70}-PCBX = 1 : 0.9$  films were obtained using a Rigaku Rotaflex with a setting of 30 kV, 100 mA, 0.01 degree steps, and a 0.2 degree min<sup>-1</sup> scan speed. Cyclic voltammograms (CV) were measured using a computer-controlled potentiostat/galvanostat (model 273A from EG&G Princeton Applied Research). A Pt disk (diameter = 2 mm) was used as a working electrode along with a Pt wire as a counter, and an Ag/AgNO3 was used as a reference electrode. For the measurements, C70-PCBXs were dissolved in a 4:1 volume mixture of o-dichlorobenzene and

acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) as a supporting electrolyte.  $Bu_4NPF_6$  was recrystallized sequentially from ethanol and ethyl acetate, then dried under vacuum prior to use. Other chemicals and acetonitrile (Aldrich, >99.8%, anhydrous, sealed under  $N_2$  gas) were used as received.

### **Results and discussion**

## Characterization of C70 derivatives

The C<sub>70</sub>-PCBR<sub>3</sub>-R<sub>9</sub> were synthesized *via* UV irradiation of [5,6]-isomers in an ODCB solution, which were prepared by a modified procedure described in the literature (Scheme 1).<sup>13,14</sup> Due to the 1,3-dipolar addition to C<sub>70</sub>, C<sub>70</sub>-PCBR<sub>3</sub>-R<sub>9</sub> consisted of a mixture of regioisomers. The <sup>1</sup>H-NMR spectrum showed distinct signals corresponding to the  $\alpha$ -protons of the ester group between  $\delta = 3.80$  and  $\delta = 4.17$  ppm, which indicated the presence of three isomers having the following content ratios; R<sub>3</sub> = 10:80:10, R<sub>5</sub> = 14:71:15, R<sub>7</sub> = 8:81:11, and R<sub>9</sub> = 9:81:10. In this study, a mixture of the C<sub>70</sub>-PCBR<sub>3</sub>-R<sub>9</sub> regioisomers was used.

Fig. 1 shows the cyclic voltammograms of  $C_{70}$ -PCBR<sub>1</sub>–R<sub>7</sub>. The first reduction potentials of  $C_{70}$ -PCBX in solution were observed at almost the same value, -0.89 V, as summarized in Table 1. This very small change in the first reduction potential was reasonable because the extended alkyl chain did not affect the conjugation length of the  $C_{70}$ -PCBX materials. Because the open circuit voltage ( $V_{oc}$ ) of the bulk-heterojunction polymer cell is determined from the difference between the HOMO level of the donor polymer and the LUMO level of the acceptor material,<sup>15</sup> the  $V_{oc}$  of solar cells comprising a blend of P3HT and  $C_{70}$ -PCBX derivatives would be nearly the same if the LUMO levels also showed a similar trend in the film state.

To characterize the synthesized fullerene derivatives, we measured the solubility of derivatives in chlorobenzene and the work function of the derivative films, as listed in Table 1. During the film drying step, the solubility is one of the most important factors (or parameters) for the formation (or self-organization) of a nanoscale morphology in the blended film. The solubility test was performed through the modified method of Troshin<sup>6</sup> as shown in ESI.<sup>†</sup> The solubility of the  $C_{70}$ -PCBX series in chlorobenzene moderately increased from



Fig. 1 Cyclic voltammograms of fullerene derivatives.

	Solubility <sup>a</sup> / mg ml <sup>-1</sup>	$E_{1/2}^{-1b}/V$	$E_{1/2}^{-2b}/V$	$E_{1/2}^{-3b}/V$	Work Function <sup>c</sup> /eV
C <sub>70</sub> -PCBR <sub>1</sub>	63	-0.90	-1.28	-1.67	-5.92
C <sub>70</sub> -PCBR <sub>3</sub>	71	-0.89	-1.27	-1.67	-5.97
C <sub>70</sub> -PCBR <sub>5</sub>	74	-0.89	-1.27	-1.67	-5.98
C <sub>70</sub> -PCBR <sub>7</sub>	88	-0.89	-1.21	-1.63	-6.04
C <sub>70</sub> -PCBR <sub>9</sub>	89	$\_^{d}$	d	$\_^{d}$	-6.00

<sup>*a*</sup> Solubility was determined in chlorobenzene solution. <sup>*b*</sup> Half way potentials were measured in the solution state with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in *o*-dichlorobenzene : acetonitrile (4 : 1) solution with the setting ferrocene-ferrocenium = +0.193 V. <sup>*c*</sup> Work functions were measured using the surface analyzer on thin films of C<sub>70</sub>-PCBXs spin-coated from chlorobenzene solution. <sup>*d*</sup> Half way potentials of C<sub>70</sub>-PCBR<sub>9</sub> could not be obtained because of its broad cyclovoltammogram.

63 mg mL<sup>-1</sup> for C<sub>70</sub>-PCBR<sub>1</sub> to 89 mg mL<sup>-1</sup> for C<sub>70</sub>-PCBR<sub>9</sub>. The work functions were measured using a surface analyzer on the films of C70-PCBXs spin-coated from a chlorobenzene solution. The work function gradually increased from  $C_{70}$ -PCBR<sub>1</sub> to  $C_{70}$ -PCBR<sub>7</sub>. The work function of the C70-PCBX derivative film corresponded to the HOMO level of each C70-PCBX in the solid state. Theoretically, if the C70-PCBX molecules are well separated from each other, as in the solution state, the HOMO level should be the same for different alkyl chain lengths. However, when the C70-PCBX molecules are sufficiently closely spaced to form aggregates or nanocrystals, the HOMO-LUMO gap of the C70-PCBX cluster would be smaller than that of the separate molecules due to dipole-dipole interactions among the closely packed  $C_{70}$ -polyhedra. Closer interactions among the  $C_{70}$ -polyhedra could lower the gap between the HOMO and LUMO levels, resulting in a decrease in the LUMO levels and an increase in

the HOMO levels. The smaller work function of  $C_{70}$ -PCBR<sub>1</sub>, measured by the surface analyzer, implies a closer molecular packing compared to the case of  $C_{70}$ -PCBR<sub>7</sub>.

## Photovoltaic properties of the devices

The polymer solar cells were fabricated with a typical sandwich structure of ITO/PEDOT:PSS/active layer/LiF/Al, and postannealing was performed at 150 °C for 30 min to improve the morphology of the active layer and the performance of the devices.<sup>18</sup> For each of the C<sub>70</sub>-PCBX acceptors, the active layer composition of the P3HT : C<sub>70</sub>-PCBX blend devices was varied from 1 : 0.7 to 1 : 1 wt ratio. We fabricated more than 24 devices in more than 6 independent batches for each composition, and the photovoltaic (PV) performance of devices fabricated from C<sub>70</sub>-PCBX comprising various alkyl lengths are presented in a statistical manner in Fig. 2 and summarized in Tables 2 and S1, ESI.†

The results showed that the short circuit current  $(J_{sc})$  and open-circuit voltage  $(V_{oc})$  significantly increased on going from  $C_{70}$ -PCBR<sub>1</sub> to the longer alkyl-substituted  $C_{70}$ -derivatives throughout the range of the P3HT :  $C_{70}$ -PCBX blend ratios; the optimum  $J_{sc}$  appeared in the cases of  $C_{70}$ -PCBR<sub>5</sub> and  $C_{70}$ -PCBR<sub>7</sub>, and the maximum  $V_{oc}$  was obtained for  $C_{70}$ -PCBR<sub>7</sub>. However, the fill factor (FF) gradually decreased as the alkyl chain length increased, and this trend became more distinct for higher content ratios of  $C_{70}$ -PCBX derivatives. Meanwhile, the overall FFs generally increased as the  $C_{70}$ -PCBX content increased in the active layer. As a result, the power conversion efficiency (PCE) is increased for longer alkyl chain lengths up to  $C_{70}$ -PCBR<sub>7</sub>, for all blend ratios, and the highest PCE reached values up to 4.3% in the P3HT :  $C_{70}$ -PCBR<sub>7</sub> blend at a ratio of 1 : 0.8.



**Fig. 2** Statistical box graphs for  $J_{sc}$ ,  $V_{oc}$ , FF, and efficiency for five  $C_{70}$  derivatives and four different  $C_{70}$ -PCBX : P3HT ratios. Each statistical box represents the data over 24 devices from more than 6 different batches.

**Table 2**Mean photovoltaic performance of P3HT :  $C_{70}$ -PCBX = 1 : 0.9devices<sup>a</sup> and roughness of P3HT :  $C_{70}$ -PCBX = 1 : 0.9 films

C <sub>70</sub> -PCBX	$J_{\rm sc}/{\rm mA~cm^{-2}}$	$V_{\rm oc}/{ m V}$	FF	PCE (%)	Ra <sup>b</sup> /nm	Rq <sup>c</sup> /nn
C <sub>70</sub> -PCBR <sub>1</sub>	9.59	0.61	0.59	3.50	0.77	1.00
C <sub>70</sub> -PCBR <sub>3</sub>	10.43	0.62	0.56	3.59	1.01	1.30
C <sub>70</sub> -PCBR <sub>5</sub>	10.57	0.64	0.57	3.84	1.17	1.47
C <sub>70</sub> -PCBR <sub>7</sub>	10.46	0.65	0.58	3.95	1.34	1.76

<sup>*a*</sup> Each device performance represents the mean value of over 24 devices. <sup>*b*</sup> Mean roughness and from AFM after annealed at 150 °C for 30 min. <sup>*c*</sup> Root mean roughness from AFM after annealed at 150 °C for 30 min.

Fig. 3 Representative IPCE spectra for  $P3HT : C_{70}$ -PCBX = 1 : 0.9 blend solar cells.

Fig. 3 shows the incident photon-to-current efficiency (IPCE) spectra for P3HT :  $C_{70}$ -PCBX blend solar cells. The overall spectral shapes were identical, irrespective of the alkyl chain length of  $C_{70}$ -PCBX. Due to the mismatch between the IPCE and the photon flux under AM 1.5 illumination, an approximate mismatch of 11% was present between the convolution and the solar simulator data.

#### Characterization of active layers

The active layers with different C70-PCBX acceptors were characterized by performing UV-Vis spectroscopic analysis, XRD, and AFM. Fig. 4a and 4b show the UV-Vis absorption spectra of  $P3HT: C_{70}-PCBX = 1:0.9$  blend films spin-coated from a chlorobenzene solution (4a) and annealed under an inert atmosphere for 30 min (4b). After the annealing process, the vibronic absorptions in the 500-600 nm region became stronger than those of the pristine film, and they increased, with small variations, as the alkyl chain length increased. This phenomenon is attributed to the presence of highly crystallized P3HT domains.<sup>16</sup> The increased crystallinity of P3HT for longer alkyl chain lengths of C70-PCBX was also confirmed by the XRD peak of the annealed P3HT :  $C_{70}$ -PCBX = 1 : 0.9 film near  $2\theta = 5.4^{\circ}$ (Fig. 5). The diffraction peak at  $2\theta = 5.4^{\circ}$  corresponded to a distance of 16 Å and was correlated with the length of the fully extended hexyl side chain of P3HT (with a length of about 13 Å).<sup>17</sup> The increased intensity indicates an increase in the



Fig. 4 UV-Visible spectra of P3HT :  $C_{70}$ -PCBX = 1 : 0.9 films spincoated on quartz form chlorobenzene solution, (a) before and (b) after thermal annealing at 150 °C for 30 min.



**Fig. 5** XRD data of P3HT :  $C_{70}$ -PCBX = 1 : 0.9 blend films annealed at 150 °C for 30 min.

crystallinity of the P3HT polymer in  $P3HT : C_{70}$ -PCBX = 1 : 0.9 film.

AFM images were recorded of the active layer surface of P3HT :  $C_{70}$ -PCBX = 1 : 0.9 devices, which were fabricated using normal device fabrication procedures with an Al cathode and annealed at 150 °C for 30 min, then the Al part was removed by immersing in a 1N HCl solution.<sup>18</sup> The RMS roughness of the interface between the Al cathode and the active layer gradually increased from 0.48 nm in  $C_{70}$ -PCBR<sub>1</sub> to 2.09 nm in  $C_{70}$ -PCBR<sub>9</sub> (see Fig. 6 and Table 2), which suggested the higher



Fig. 6 AFM phase images (top) and topological images (bottom) of P3HT :  $C_{70}$ -PCBX = 1 : 0.9 blend films annealed at 150 °C for 30 min.

self-organization of P3HT in the longer alkyl chain acceptor. The AFM phase images shown in Fig. 6 demonstrated that P3HT-rich and  $C_{70}$ -PCBX-rich domains in all films were well separated, and this clear phase separation was helpful for charge percolation.

The UV-Vis, XRD, and AFM data all suggested the same result, that the phase segregation in the P3HT : C70-PCBX blended active layer was enhanced by the increase in alkyl length of the C70-PCBX molecules after annealing. This trend was correlated with the measured solubilities of C70-PCBX in chlorobenzene, given in Table 1. According to Heeger et al.,11 additions of a small quantity of a high boiling point component to the blend of the low band gap polymer PCPDTBT/PCBM solution yielded a more segregated PCPDTBT/PCBM film during the film forming and spin-coating processes, which resulted in better charge percolation properties. This phenomenon was caused by the selective solubilization of the fullerene component by the high boiling point additives. In this work, although the additive was not used in the blend solution, better phase segregation appeared to have been obtained using the longer alkyl substituted C70-PCBX compounds. C70-PCBR1 had higher solubility than P3HT.6 Elongation of the alkyl chain enhanced the solubility of  $C_{70}$ -PCBR<sub>3</sub>-R<sub>9</sub> in chlorobenzene, and the solubility gap with P3HT becomes wider. Therefore, the P3HT polymer solidified at an early stage of the film forming process, and much of the C70-PCBX derivative was retained in the reduced chlorobenzene solution in a concentrated form due to the high solubility of C<sub>70</sub>-PCBX in chlorobenzene. Finally, the P3HT polymer and C70-PCBX in blended solutions had a higher tendency to selforganize, and a highly concentrated C<sub>70</sub>-PCBX solution thereby solidified, resulting in percolation pathways.

The overall spectral shapes of the IPCE spectra were identical, irrespective of the alkyl chain length of  $C_{70}$ -PCBX, as shown in Fig. 3. This suggested that the photocurrent difference at each wavelength as a function of the alkyl chain length was not caused by differences in the photo-absorption, but was mainly due to differences in charge percolation. Therefore, the reason for a higher  $J_{sc}$  near  $C_{70}$ -PCBR<sub>5</sub> and  $C_{70}$ -PCBR<sub>7</sub> may have originated from the optimal domain sizes of the P3HT :  $C_{70}$ -PCBX layer.

The cyclic voltammograms of  $C_{70}$ -PCBX in the ODCB : CH<sub>3</sub>CN (4 : 1) solution indicated that the first reduction potentials, the LUMO levels of the C<sub>70</sub>-PCBX acceptors, yielded almost the same value, -0.89 V, setting the ferrocene-ferrocenium oxidation potential at +0.193 V as a reference.

However, the PV devices fabricated using this  $C_{70}$ -PCBX series revealed a gradual increase in  $V_{oc}$  from  $C_{70}$ -PCBR<sub>1</sub> to  $C_{70}$ -PCBR<sub>7</sub>, where P3HT was used as a common donor polymer. This suggested that the electronic properties of  $C_{70}$ -PCBX in a solid form inside the active layer were apparently different from those in solution.

It seems natural to assume that the larger  $V_{\rm oc}$  for C<sub>70</sub>-PCBR<sub>7</sub> was related to the higher LUMO level due to the relatively looser packing of C<sub>70</sub>-PCBR<sub>7</sub> molecules compared to the cases of shorter alkyl chains. In addition, the fullerene derivatives with longer alkyl chains are possibly more hindered, resulting in reduced electronic coupling with the P3HT polymer. According to Vandewal *et al.*, as shown in eqn (1), reductions in the electronic coupling between the polymer and the fullerene would suppress the charge-transfer band oscillator strength and would reduce  $J_0$ , and thus increase  $V_{\rm oc}$ .<sup>19</sup>

$$V_{\rm oc} = \frac{kT}{q} \ln \left( \frac{J_{\rm sc}}{J_{\rm o}} + 1 \right) \tag{1}$$

Here, k is the Boltzmann constant, T is the absolute room temperature, q is the elementary electron charge and  $J_0$  is the dark saturation current.

With a further increase in the alkyl chain length to  $C_{70}$ -PCBR<sub>9</sub>, all solar cell parameters are lower than  $C_{70}$ -PCBR<sub>7</sub>, even with the highest P3HT crystallization. No clear morphological differences were observed in the AFM images (Fig. 6). This charge deterioration may have been caused by excessive intermolecular distance within or between  $C_{70}$ -PCBR<sub>9</sub> aggregates resulting from alkyl chains that were too long.

#### Mixing properties from the results of a computational calculation

To understand the intermixing behavior between P3HT and  $C_{70}$ -PCBX acceptors, we adopted the Blends (Accelrys<sup>®</sup>) program,<sup>20</sup> which combines a modified Flory-Huggins model<sup>21</sup>

and molecular simulation techniques. These calculations estimated the compatibility of binary mixtures.

The chi-parameter,  $\chi$ , is the interaction parameter defined as shown in eqn (2). The traditional Flory-Huggins model describes each component as occupying a lattice site. For a lattice with a coordination number Z, the mixing energy is represented by eqn (3).

$$\chi = \frac{E_{\text{mix}}}{RT} \tag{2}$$

$$E_{\rm mix} = \frac{1}{2}Z(E_{\rm bs} + E_{\rm sb} - E_{\rm bb} - E_{\rm ss})$$
(3)

where  $E_{\text{mix}}$  is the mixing energy, T is the absolute temperature, R is the gas constant, and  $E_{ij}$  is the binding energy between a unit of component i and a unit of component j.

To perform a Blends calculation, the 3-hexylthiophene unit was used as a base and the C<sub>70</sub>-PCBX molecules were used as screens. Geometry-optimized structures of each 3-hexylthiophene repeating unit and C<sub>70</sub>-PCBX were optimized using a density function theory (DFT) quantum mechanical molecular modeling program (DMol<sup>3</sup> in the Materials Studio 5.0 package, Accelrys<sup>®</sup>)<sup>22</sup> with symmetry restrictions, as shown in the supplementary data, Fig. S3.† In the previous section, we assumed that the aggregation and/or segregation of the active material was affected by the interactions with the solvent during the film-forming process. However, in the Blends calculation, only the interactions between the active components were considered, and the solvent effect was ignored. The Blends calculation results obtained using a Dreiding force field are summarized in Table 3.

The positive values of  $\chi$  for blending between P3HT and C<sub>70</sub>-PCBXs indicated that both molecules preferred to be surrounded by similar components, rather than intermixing. The  $\chi$  parameter gradually increased in going from C<sub>70</sub>-PCBR<sub>1</sub> to C<sub>70</sub>-PCBR<sub>7</sub>, then decreased for C<sub>70</sub>-PCBR<sub>9</sub>. This calculation correlated well with the segregated morphology of the active layer, as confirmed by UV-Vis spectroscopy, XRD, and the AFM. According to the Blends calculation, the main cause of the increased  $\chi$  parameter value for C<sub>70</sub>-PCBR<sub>7</sub> was the increase in the binding energy of C<sub>70</sub>-PCBX itself (*E*<sub>ss</sub>) rather than in the binding energy change between P3HT and C<sub>70</sub>-PCBX (*E*<sub>bs</sub>) or P3HT itself (*E*<sub>bb</sub>).

Table 3 Mixing properties of P3HT and C70-PCBXs.<sup>a</sup>

Screen	$\chi^b$	$E_{\min}{}^{c}/kcal ^{-1}$	$E_{\rm bb}$ avg. <sup>d</sup> /kcal mol <sup>-1</sup>	$E_{\rm bs}$ avg. <sup>d</sup> /kcal mol <sup>-1</sup>	$E_{\rm ss}$ avg. <sup>d</sup> /kcal mol <sup>-1</sup>	$Z_{bs}^{e}$
C <sub>70</sub> -PCBR <sub>1</sub>	33.10	19.60	-3.07	-6.19	-16.20	3.85
C <sub>70</sub> -PCBR <sub>3</sub>	32.38	19.17	-3.07	-6.21	-16.18	3.67
C <sub>70</sub> -PCBR <sub>5</sub>	41.27	24.44	-3.09	-6.31	-18.23	3.77
C <sub>70</sub> -PCBR <sub>7</sub>	56.01	33.17	-3.08	-6.30	-21.43	3.59
C <sub>70</sub> -PCBR <sub>9</sub>	42.14	24.96	-3.08	-6.32	-18.58	3.51

<sup>*a*</sup> P3HT is used as a base material and all values were obtained at 298 K. <sup>*b*</sup> Interaction parameter. <sup>*c*</sup> Mixing energy. <sup>*d*</sup> Average binding energy of a base-base pair ( $E_{bb}$ ), base-screen pair ( $E_{bs}$ ) and screen-screen pair ( $E_{ss}$ ). <sup>*e*</sup> The coordination number,  $Z_{bs}$ , is the number of screen molecules ( $C_{70}$ -PCBX) that can be packed around a single repeating unit of base material (P3HT).

## Conclusions

Extended alkyl chains of the C70-derivatives increased the phase segregation and interface roughness in bulk heterojunction polymer solar cells with P3HT as a donor polymer. These effects were caused by the enhanced solubility and increased molecular binding energy of C70-PCBX itself with longer alkyl chains. A moderate phase segregation was thought to enhance the nanomorphology in the active layer of the device, resulting in improved charge percolation, as evidenced by the higher  $J_{sc}$  and  $V_{\rm oc}$  of the C<sub>70</sub>-PCBR<sub>5</sub>-R<sub>7</sub> samples. However, in the case of an excessively long alkyl chain, such as that in C70-PCBR9, all solar cell parameters deteriorated, possibly due to poorer charge transport across the excessively long intermolecular distance. Through preparation of a series of C<sub>70</sub>-PCBX acceptor materials, we have tested the P3HT polymer. A more meaningful application would be to introduce new amorphous low band gap polymers, which may require effective phase segregation without further treatments, and they may require complementary absorption of shorter wavelengths by the C70 moiety.

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