

Fine-tuning of Polymer Photovoltaic Properties by the Length of Alkyl Side Chains^{*}

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Abstract This paper reports the synthesis and characteristics of a series of alkyl-substituted planar polymers. The physical properties are carefully tuned to optimize their photovoltaic performance. Depending on the length of soluble alkyl side chains which modify the structural order and orientation substantially in polymer backbones, the device performance can be improved significantly. The tuning of HOMO energy levels optimized polymers' spectral coverage of absorption and their hole mobility, as well as miscibility with fullerene; all these efforts enhanced polymer solar cell performances. The short-circuit current, J_{sc} for polymer solar cells was increased by adjusting polymer chain packing ability. It was found that films with well distributed polymer/fullerene interpenetrating network exhibit improved solar cell conversion efficiency. Enhanced efficiency up to 5.8% has been demonstrated. The results provide important insights about the roles of flexible chains in structure-property relationship for the design of new polymers to be used in high efficient solar cells.

Keywords: Polymer solar cells; Alkyl side chains; Morphology; Charge mobility.

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INTRODUCTION

Polymer-based organic photovoltaic systems hold the promise for a cost-effective, light-weight solar energy conversion platform, which could benefit from simple solution processing of the active layer. Bulk heterojunction (BHJ) concept solar cells are of the most successful device structures^[1–3]. Efficient single molecule solar cells are another hot spot^[4]. In recent work, the solar cells made great progress in cell efficiency promotion, the power conversion efficiency record broke through continually by new polymers^[5–7]. Power conversion efficiencies (PCE) higher than 9% has been achieved^[8–11]. Chemists understand the principle and use new strategies to improve BHJ solar cells efficiency. Reducing the band gap of polymers can harvest more sunlight to obtain higher short-circuit currents (J_{sc})^[12–14]. A significant strategy is to increase the open-circuit voltage (V_{oc}) by lowering the highest occupied molecular orbital (HOMO) of the donor polymer and by raising the lowest unoccupied molecular orbital energy level of the acceptor^[15–18]. However, parameters must be

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synergistically optimized. Achieving both a higher J_{sc} and a higher V_{oc} is critical to the device performance. To realize this goal, different solubilizing alkyl chains have the substantial effect. Flexible side chains are less developed and usually used only as solubilizing groups^[19]. The incorporation of flexible side chains in the structures of different conjugated polymers is now still a common way of improving processability by increasing solubility or fusibility and side chains also stabilize the cation radicals by electron-releasing effects^[20]. However, the position of the side chains also affects the morphology and crystallization of the blend of polymer/ C_{70} fullerene derivative in films, even the same side chains on different positions^[21]. In this paper we tailed the alkyl group of various lengths on to the same conjugated polymer backbone at same position and it gave surprise achievement. Generally, the energy levels of polymers depend on the chemical nature of donor and acceptor units^[22]. However, we found the HOMO or LUMO level changed according to the length of alkyl groups. A proper length of alkyl groups results in a closer distance between the main chains and thus forms “H” type face to face aggregation. The more closer aggregation gives higher hole mobility for solid films. Maximizing the short-circuit current in a low-band gap planar polymer is one of the critical factors towards enabling high-efficiency solar cells. Coplanarity in the conjugated backbone is crucial for electron delocalization, which requires a minimal torsional bond angle because *p*-orbital overlapping occurs effectively in the planar structure^[23]. We optimized all these factors resulting in high performance of the device. The average of five solar cells based on poly(2-(5-(5,6-bis(dodecyloxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-dodecyl-9H-carbazole) (C-12) (Fig. 1) blended with $PC_{71}BM$ gave a short-circuit current (J_{sc}) of 11.8 mA/cm², an open-circuit voltage (V_{oc}) of 0.81 V, a fill factor (FF) of 0.60 and a PCE of 5.8% under AM1.5 (100 mW/cm²). A 11.8 mA/cm² of J_{sc} indicates that C-12: $PC_{71}BM$ has a balanced charge transport, which makes C-12 a very promising polymer for solar cell application contrast to poly(2-(5-(5,6-bis(octyloxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-octyl-9H-carbazole) (HXS-1, named C-8 in this paper). At first we were rather puzzled by this peculiar property until recently, You *et al.* published their work^[24]. They also observed this “anti- conventional wisdom” phenomenon. All the synthesized polymers have proper molecular weight and good thermal property. Thermo gravimetric analysis shows that the polymers exhibit good stability up to 300 °C. DSC experiments reveal a high glass transition temperature above 100 °C for all the polymers except 96 °C for poly(2-(5-(5,6-bis(methoxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-methyl-9H-carbazole) C-1 (shown in supporting information).

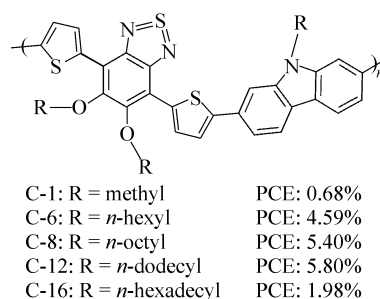


Fig. 1 The molecular structure of polymers and photovoltaic performance

EXPERIMENTAL

Materials and Instruments

$PC_{71}BM$ was purchased from Nano-C and used as received. Other materials were commercially available and used without further purification. Tetrahydrofuran (THF) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Chloroform was distilled before use. ¹H- and ¹³C-NMR spectra were measured using a Bruker AV400 spectrometer. Absorption spectra were taken using a Shimadzu model UV-3600 spectrophotometer. The electrochemical behavior of the compounds was investigated using cyclic voltammetry (IviumStat A25361) with a standard three-electrode electrochemical cell in a 0.1 mol/L

tetrabutylammonium hexafluorophosphate solution in CH_3CN at room temperature under atmosphere of nitrogen with a scanning rate of $100 \text{ mV}\cdot\text{s}^{-1}$. A glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgNO_3 (0.01 mol/L in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis TGA and differential scanning calorimetry (DSC) measurements were carried out under a nitrogen atmosphere at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ on a Pyris-1 TGA and a TA 2910. Powder X-ray diffraction (XRD) patterns were obtained by $\text{Cu K}\alpha$ radiation on a PANalytical X' Pert PROMPD diffractometer. Hole mobility was obtained by testing organic field effect transistor (FET). The thin film organic field-effect transistors (OFET) of all polymers were prepared by spin-coating method. Each polymer with the concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$ in *o*-dichlorobenzene (DCB) was spun on OTS-treated Si/SiO_2 substrates. Au electrodes were thermally deposited through a multiple finger configuration mask with channel length $50 \mu\text{m}$ and width $2500 \mu\text{m}$. Measurements were performed in air using a Keithley 4200-SCS semiconductor parameter analyzer and a Micromanipulator 6150 probe station in a clean and shield box.

Fabrication and Characterization of PSCs

The photovoltaic properties of all polymers were investigated in the device structure ITO/PEDOT:PSS/polymer: [6, 6]-phenyl- C_{71} -butyric acid methyl ester (PC_{71}BM)/LiF/Al. The active layers were spin-coated from chlorobenzene (CB), acceptors (1:3 wt ratio, $7 \text{ mg}\cdot\text{mL}^{-1}$ for each), and a small amount of the high boiling-point additive 1, 8-diiodooctane (DIO) 2.5% (*V/V*) was used in order to optimize the morphology. The solution was then spin-coated on indium tin oxide (ITO)/glass substrates with a precoated poly(ethylenedioxy thiophene): polystyrene sulfonate (PEDOT:PSS) layer (about 40 nm). The thickness of the photoactive layer is in the range of 90–120 nm. A bilayer cathode consisting of a LiF layer (0.5 nm) and subsequently an aluminum layer (100 nm) was deposited by thermal evaporation under vacuum ($1.33 \times 10^{-10} \text{ MPa}$). The device active area is $\sim 0.04 \text{ cm}^2$ for all the solar cell devices discussed in this work. Device characterization was done in air without encapsulation under simulated AM 1.5G irradiation ($100 \text{ mW}\cdot\text{cm}^2$) using a xenon-lamp-based solar simulator immediately after the devices were fabricated in glove box. The external quantum efficiency (EQE) measurements of the devices were performed in air (PV Measurements Inc., model QEX7).

General Procedures for the Preparation of Polymers

The synthesis procedure of different polymers is similar to HXS-1 (see our previous work) Fig. 1^[5]. Poly(2-(5-(5,6-bis(methoxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-methyl-9H-carbazole) C-1: 4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(methoxy)benzo-[c][1,2,5]-thiadiazole (0.2 g, 0.38 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-methyl-9H carbazole (0.167 g, 0.38 mmol), NaHCO_3 (0.6 g, 7.14 mmol), H_2O 3 mL, THF 30 mL, $\text{Pd}(\text{PPh}_3)_4$ (45 mg). 54 mg (yield 26%) of C-1 was obtained. $^1\text{H-NMR}$ (400 MHz, CDCl_3): (δ) 8.69–8.52 (m, 2H), 8.11–8.09 (m, 2H), 7.91–7.44 (m, 6H), 4.16–3.97 (m, 6H). Element Analysis for $[\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_2\text{S}_3]_n$: Calcd.: C, 49.94; H, 2.75; N, 6.02. Found: C, 49.20; H, 4.03; N, 6.01.

Poly(2-(5-(5,6-bis(hexyloxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-hexyl-9H-carbazole) C-6: 4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(hexyloxy)benzo-[c][1,2,5]-thiadiazole (0.5 g, 0.76 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-hexyl-9H-carbazole 0.38 g (0.76 mmol), NaHCO_3 (1.2 g, 14 mmol), H_2O (6 mL), THF (50 mL), $\text{Pd}(\text{PPh}_3)_4$ (8 mg). 370 mg (yield 64%) of C-6 was obtained. $^1\text{H-NMR}$ (400 MHz, 1, 2-dichlorobenzene- d_4): (δ) 8.92 (m, 2H), 8.15 (m, 2H), 7.80 (m, 6H), 4.35 (m, 6H), 2.20 (m, 4H), 1.98 (m, 2H), 1.60–1.30 (m, 18H), 0.94 (m, 9H). Elemental Analysis for $[\text{C}_{46}\text{H}_{55}\text{N}_3\text{O}_2\text{S}_3]_n$ (%): Calcd.: C, 70.55; H, 7.24; N, 5.48. Found: C, 67.92; H, 7.16; N, 5.32.

Poly(2-(5-(5,6-bis(dodecyloxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-dodecyl-9H-carbazole) C-12: 4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo-[c][1,2,5]-thiadiazole (0.4 g, 0.58 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-dodecyl-9H carbazole (284 mg, 0.58 mmol), NaHCO_3 (1.2 g, 5.6 mmol), H_2O (6 mL) THF (80 mL), $\text{Pd}(\text{PPh}_3)_4$ (12 mg). 452 mg (yield 60%) of C-12 was obtained. $^1\text{H-NMR}$ (400 MHz, 1, 2-dichlorobenzene- d_4): (δ) 8.92 (m, 2H), 8.15 (m, 2H), 7.80 (m, 6H),

4.41–4.24 (m, 6H), 2.00 (m, 4H), 1.59 (m, 6H), 1.60–1.30 (m, 54H), 0.94 (m, 9H). Elemental Analysis for $[C_{76}H_{91}N_3O_2S_3]_n$ (%): Calcd.: C, 77.70; H, 7.81; N, 3.58. Found: C, 67.92; H, 7.16; N, 5.32.

Poly(2-(5-(5,6-bis(hexadecyloxy)-4-(thiophen-2-yl) benzo[c][1,2,5] thiadiazol-7-yl) thiophen-2-yl)-9-hexadecyl-9H-carbazole) C-16: 4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(hexadecyloxy)benzo-[c] [1,2,5]-thiadiazole (0.3 g, 0.32 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-hexadecyl-9Hcarbazole (0.21 g, 0.32 mmol), $NaHCO_3$ (0.6 g, (2.8 mmol), H_2O (3 mL), THF (30 mL), $Pd(PPh_3)_4$ (6 mg). 240 mg (yield 54%) of C-16 was obtained. ^1H -NMR (400 MHz, 1,2-dichlorobenzene- d_4): δ 8.92 (m, 2H), 8.15 (m, 2H), 7.80 (m, 6H), 4.41–4.24 (m, 6H), 2.00 (m, 4H), 1.59 (m, 6H), 1.60–1.30 (m, 78H), 0.94 (m, 9H). Elemental Analysis for $[C_{76}H_{91}N_3O_2S_3]_n$ (%): Calcd.: C, 79.43; H, 8.33; N, 3.02. Found: C, 75.56; H, 9.12; N, 3.52.

RESULTS AND DISCUSSION

Optical and Physical Properties of the Polymers

Absorption is a very important property for the photovoltaic materials especially in the visible region. Figure 2 shows the UV-Vis absorption spectra of C-1, C-6, C-8, C-12 and C-16 in solvent and solid film state. For solid film samples, the long-wavelength maximum absorption peak shifts for C-1 (methyl side chain) 514 nm to C-6 (hexyl) 546 nm and C-8 (octyl) 561 nm and goes a step further to 582 nm for C-12 (dodecyl), then back shift to 536 nm for C-16 (hexadecyl). Similar behavior was observed in solution for the short-wavelength peak band. See Table 1. It can be seen that the wavelength of the absorption peaks reaches maxima for C-12 (dodecyl) in both solid film and solvent forms. There are two absorption bands: one at 300–450 nm, which we assign to localized π - π^* transitions; and another broader band from 450 to 700 nm in the long wavelength region, corresponding to intramolecular charge transfer (ICT) between the acceptor (BT) and donor (thiophene carbazole derivatives) units. For C-1, the conjugated chain units are ~5 mers calculated according to the gel permeation chromatography (GPC) data (supporting information, table S1). It is very short contrasted to C-8 (61mers) and C-12 (36mers). The blue shift of the absorption peaks for C-1 may well be caused by its relatively short conjugated chain. As compared to other polymers, the interchain association band for C-12 still remains at a higher relative intensity than that for C-8 and C-16. This absorption behavior indicates that C-12 aggregates in solution more strongly than the other analogues. In the PL spectra C-12 has the largest blue shift. The smallest stock shift is attributed to the aggregation of the polymer chains in the solid state. (Table 1). The presence of vibronic features in the photoluminescence spectrum of polymer further corroborates more ordering of the polymer C-12 in film state. We believe that this phenomenon was affected by more ordering of the polymer C-12 in film state. We believe that this phenomenon was affected by closer back-bone molecular distance (see Fig. 3b). All copolymer powders were analyzed by X-ray diffraction (Fig. 3b). In the XRD spectra, there are two peak bands. It suggests a lamellar packing for these polymers^[25]. For all polymers, the peak d_1 corresponds to a layering distance between sheets of each one of polymer chains that are packed in the plane, perpendicular to their longitudinal axes^[26]. The second broader peak d_2 could be attributed to the distance between the polymer chains within the layered planes^[27]. For C-1 with the shortest alkyl group, the second peak d_2 clearly reveals that the distance between polymers main chains plane are ~0.35 nm. This means that it has the closest molecular distance and strong dipole-dipole and π - π interactions induced by the benzothiadiazole unit. However, C-1 is almost insoluble in organic solvents and difficult to form uniform films. So it is not suitable for solution process. For C-16 with the longest alkyl group, peak d_2 reveals the distance ~0.43 nm, the largest space distance between polymer mainchains. It has weakest π -overlapping interactions. Except for the C-12 ($d_2 \approx 0.38$ nm), there is a regular change according to the length of alkyl group. The plane spacing becomes larger as the length of the side chains increases. The polymer C-12 breaks this rule. It shows a shorter distance (0.38 nm) than C-8 (0.39 nm) (with octyl side chain) or C-6 (0.40 nm) (with hexyl side chain). This indicates that C-12 has a closer distance between molecules than the other polymers. Another group of sharp XRD peaks for the polymers is at smaller 2θ position. $d_1 \approx 0.81$ nm for C-1; $d_1 \approx 1.56$ nm for C-6; $d_1 \approx 1.69$ nm for C-8; $d_1 \approx 2.54$ nm for C-12; $d_1 \approx 3.17$ nm for C-16. In fact, it is fair to assume that this d_1 value is attributed to the distance between polymer main chains^[28].

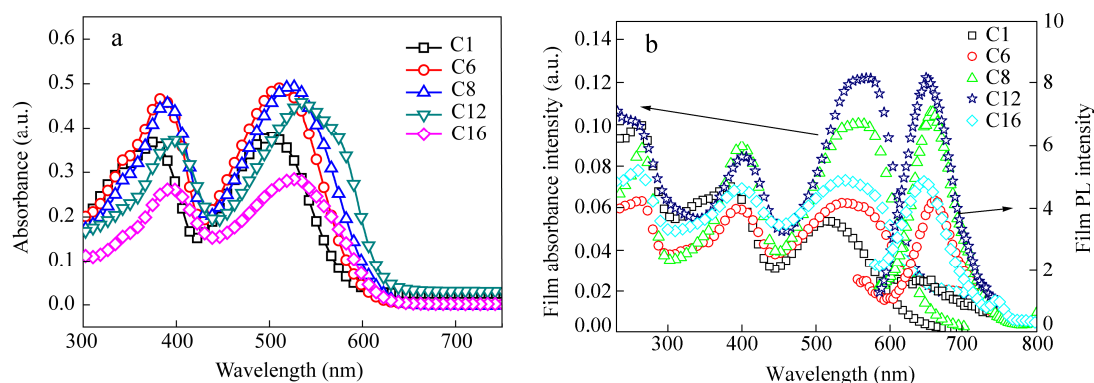


Fig. 2 Solution (a) and thin film (b) UV-Vis absorption-PL spectra of polymers. Solution measurements were done in dilute CHCl_3 (concentration: $8.4 \times 10^{-3} \text{ mg} \cdot \text{mL}^{-1}$). Thin films were spin coated from a $5 \text{ mg} \cdot \text{mL}^{-1}$ solution in chlorobenzene.

Table 1. Summary of absorption, emission, optical band gap and HOMO level of polymers

Polymers	Absorption in CHCl_3 λ_{max} (nm)	Absorption in film λ_{max} (nm)	Emission in film λ_{max} (nm)	Stokes shift (nm)	Band gap	HOMO (eV)	LUMO (eV)
C-1	501	514	654	140	1.99	-5.20	-3.21
C-6	512	546	661	115	1.95	-5.24	-3.29
C-8	524	561	657	96	1.90	-5.22	-3.32
C-12	536	582	650	68	1.95	-5.44	-3.49
C-16	528	536	647	111	1.95	-5.28	-3.33

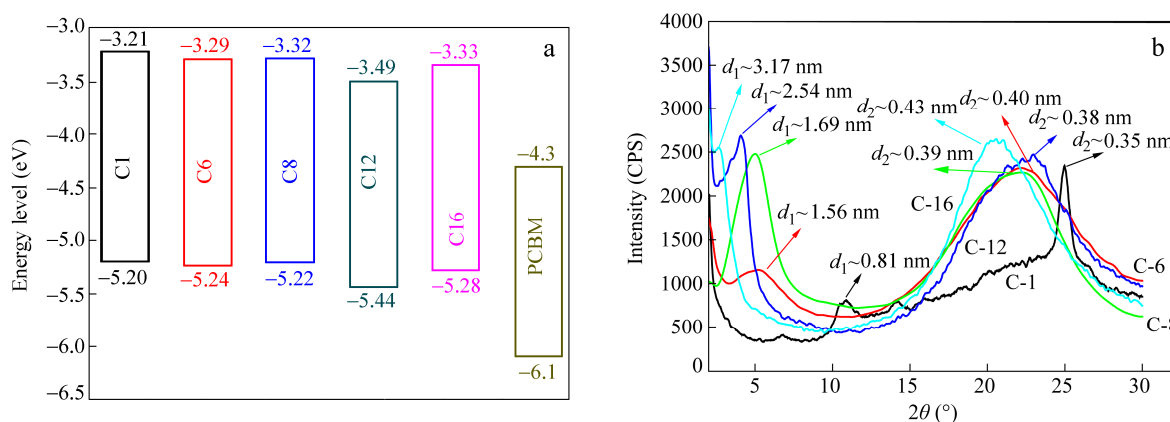


Fig. 3 (a) Energy level of different polymers and PCBM; (b) X-ray diffraction patterns

Energy level and Physical Properties

It is generally believed that the side alkyl chains have minimal impact on the electrochemistry of the polymers. We observed that the length of side alkyl chains often changes the polymers energy level. Cyclic voltammetry (CV) was carried out to determine the electrochemical highest occupied molecular orbital (HOMO) levels (Figure S6 in Supporting Information). All the polymers have similar band gap values. But the HOMO level shifts from -5.20 eV (C-1) to -5.44 eV (C-12) and then back upraise to -5.28 eV (C-16) (Table 1, Fig. 3a). C-12 has the lowest HOMO level value. We know lower HOMO level value will increase the V_{oc} . Since V_{oc} is determined by the difference between the PCBM's E_{LUMO} and the polymer's E_{HOMO} levels^[29, 30]. We didn't obtain the obviously large voltage at the best cells performance, which is affected by the difficult precise thickness control of LiF interlayer as expected. Increase the side chains length would decline the E_{HOMO} level. However, the C-12 breaks this law. We attribute this to the strong π over lapping among individual conjugated polymer

chains (see Fig. 3b). We believe that C-1 tends to be oxidized than C-12 though it has the closest molecular distance of ~ 0.35 nm. The reason is as follows. 1. The oxidation occurs on the conjugated main chain, alkyl side chains will protect this occurrence in film and C-1 only could form very poor quality films. 2. C-1 has a very low molecular weight, M_w : 3112, only 5–7 chain units; C-12, M_w : 36003, ~ 36 chain units. Small molecule is easy to be oxidized than the larger one. The larger molecular weight and closer distance in solid film state result in more difficult oxidation. So C-12 has a special HOMO and LUMO level. There is a proper side alkyl chains length attached to the same main chains to obtain an optimal polymer which can achieve higher device performance. The polymer C-12 is it. C-12 has a more broad absorbance spectra and a proper energy level indicating that it is a promising donor materials for PSCs. Fréchet *et al.* modulated the size and branching of the alkyl substituent appended to *N*-alkylthieno[3,4-*c*]pyrrole-4,6-dione TPD while preserving the π -conjugated backbone structure and also achieved enhanced 6.8% PCE^[31].

Nanoscale Morphology

Nanoscale morphology of different polymers/PCBM is critical to understand the interaction between polymers and PCBM as well as their solar cell performance, because both the charge generation and recombination depend strongly on the morphology of active layer^[32]. The morphology was investigated by atomic force microscopy (AFM) using tapping mode. We can see the formation of an interpenetrating bicontinuous network between polymer C-8, C-12 and PCBM with an ideal domain size of ~ 10 – 20 nm and this is crucial for charge generation and transportation^[33]. For bulk heterojunction polymer solar cells, moderate phase separation is a practical way to form bicontinuous donor-acceptor penetrating network. Homogeneous and bicontinuous distribution of the polymer and fullerene domains plays a more important role in photovoltaic properties than smoothness of the active layer surface^[34]. Figure 4 shows that C-1/PCBM even can't form a fine film. The root mean square roughness (RMS) is ~ 9.5 nm. C-6/PCBM film has a fibril phase separation with a RMS ~ 11.0 nm. The highest external quantum efficiency (EQEs) and PCEs are closely related to fibril widths of polymers as formed in films^[35]. C-6-based BHJ solar cell got high EQEs but low fill factor because of wide fibril.

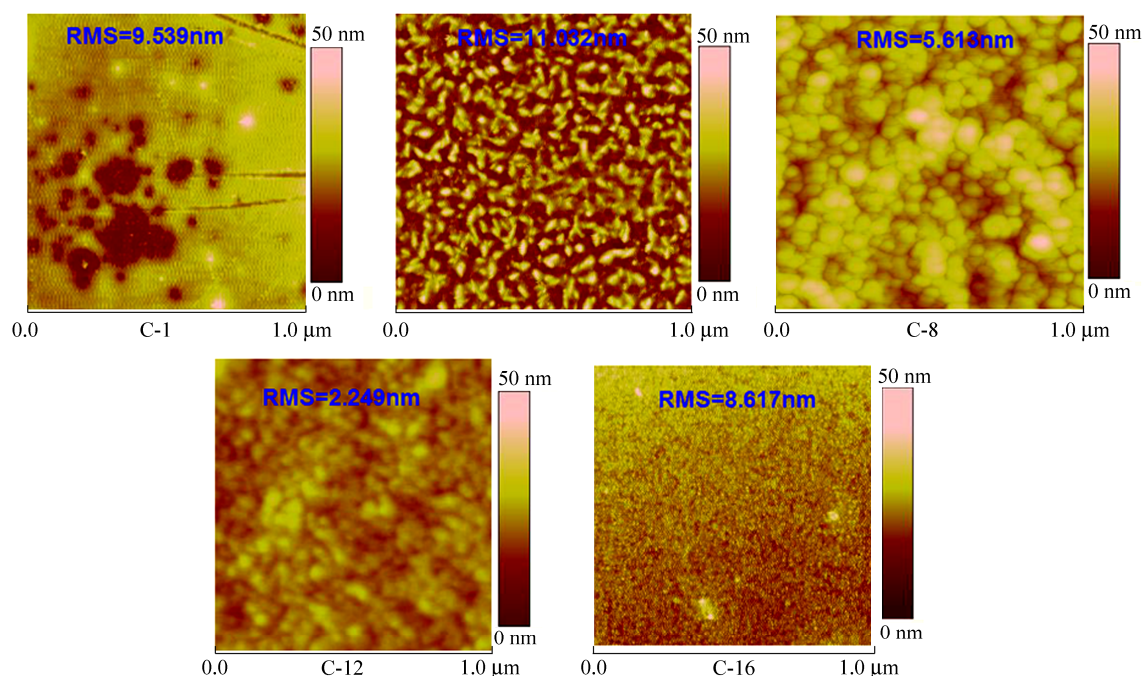


Fig. 4 AFM height images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of different polymers/PC₇₁BM (1:3, *W/W*) blend films spin coated from DCB: (a) C-1, (b) C-6, (c) C-8, (d) C-12 and (e) C-16

Field Effect Transistor (FET) Mobility Measurements

For all copolymers field effect transistor (FET) was used to test their charge mobility properties. Pei *et al.* found farther branched alkyl chains can effectively decrease interchain π - π stacking distance and improve carrier mobility of the Isoindigo-based conjugated polymers^[36]. In this work, we found that a proper length of the flexible branchless alkyl chains attached to same main chain gave the largest carrier mobility. Table 2 showed that C-12 has the highest hole mobility which is three times larger than that for C-8. It is very difficult to form a fine film of C-1. So in several devices we couldn't detect its mobility. We all know higher mobility allows charge to transfer a longer distance so that the thickness of the active layer can be appropriately increased. More solar energy would transfer to electrical current.

Table 2. Photovoltaic properties and average charge mobilities of pure polymers

Pure polymer	C-1	C-6	C-8	C-12	C-16
Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Very low	1×10^{-4}	1×10^{-4}	3×10^{-4}	1×10^{-5}
Thickness (nm)	87	93	100	105	97
J_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	2.9	12	9.6	11.8	5.5
V_{oc} (V)	0.70	0.81	0.81	0.81	0.80
Fill factor	0.33	0.47	0.69	0.60	0.51
PCE (AFM = 1.5)	0.68%	4.59%	5.40%	5.80%	1.98%

Photovoltaic Properties of Polymers

The J - V curves are shown in Fig. 5(a), and the average device parameters are listed in Table 2. It is clear that C-12 possesses optimized J_{sc} and V_{oc} value so that the highest PCE is achieved. Too short or too long side chains would result in poor film morphology of the blends or weaken the intermolecular interaction, leading to a small J_{sc} . (for example, C-1 and C-16). Our library of five polymers shares an identical conjugated backbone so that the variation of different side chains is believed to represent the strength of the intermolecular interaction in the polymer/PCBM blends in thin films. Straight side chains with 6–12 methenes would promote the intermolecular interaction, rendering a large J_{sc} . (for example, C-6, C-8 and C-12). External quantum efficiency (EQE) curves of PSCs based on all polymers are shown in Fig. 5(b). The J_{sc} values calculated from the integration of EQEs agree roughly with the J_{sc} values obtained from the J - V measurements.

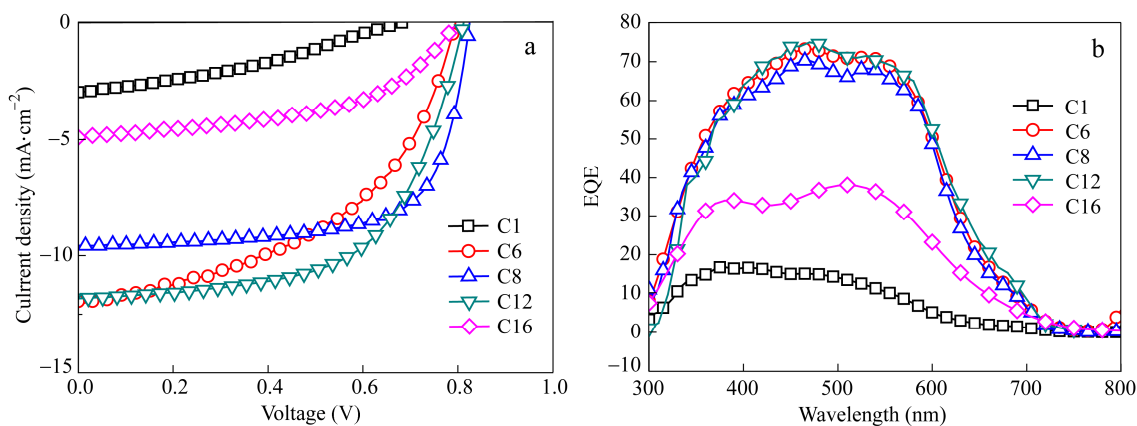


Fig. 5 Current density-voltage curves (a) of optimized solar cells of the polymers with [70]PCBM and (b) EQE of the same devices

CONCLUSIONS

In conclusion, we report the synthesis and device performance of a series of polymers with straight alkyl side chains. The polymers PCE ranges from 0.68% to 5.8%, that was depending on the length of the side chains alkyl group. We demonstrated the solubilizing group's length in same polymer back-bones impacts structural order and orientation. The side chain length critically affects the polymer energy level and film charge mobility. The

length of linear alkyl side chains determines the strength of the intermolecular interaction in thin films of the polymer/PCBM blends therefore remarkably affects film morphology and consequently optical, electrochemical, charge transport and photovoltaic properties of the D-A conjugated copolymers. In terms of OPV performance, octyl and dodecyl side chains lead to very desirable surface morphology in this polymer class and extremely good device PCEs. Our results provide important idea for the future design of new polymeric molecular structure to be used in high efficient solar cells.

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REFERENCES

- 1 Wang, Y., Yang, F., Liu, Y., Peng, R., Chen, S. and Ge, Z., *Macromolecules*, 2013, 46: 1368
- 2 Wang, Y., Liu, Y., Chen, S., Peng, R. and Ge, Z., *Chem. Mater.*, 2013, 25: 3196
- 3 Qin, R.P., Song, G.L., Jiang, Y.R. and Bo, Z.S., *Chem. J. Chin. Univ. Chin.*, 2012, 33: 828
- 4 Qu, J.F., Liu, J., Li, S.D., Xie, Z.Y. and Geng, Y.H., *Chinese J. Polym. Sci.*, 2013, 31(5): 815
- 5 Yuan, Y., Reece, Sharma, T.J., Poddar, P.S., Ducharme, S., Gruverman, A., Yang, Y. and Huang, J., *Nat. Mater.*, 2011, 10: 296
- 6 Qin, R., Li, W., Li, C., Du, C., Veit, C., Schleiermacher, H.F., Andersson, M., Bo, Z., Liu, Z., Inganäs, O., Wuerfel, U. and Zhang, F., *J. Am. Chem. Soc.*, 2009, 131: 14612
- 7 Park, S.H., Roy, A., Beaupre, S., Cho, S., Coates, N., Moon, J.S., Moses, D., Leclerc, M., Lee, K. and Heeger, A.J., *Nat. Photon.*, 2009, 3: 297
- 8 Li, K., Li, Z., Feng, K., Xu, X., Wang, L. and Peng, Q., *J. Am. Chem. Soc.*, 2013, 135: 13549
- 9 Li, W., Furlan, A., Hendriks, K.H., Wienk, M.M. and Janssen, R.A.J., *J. Am. Chem. Soc.*, 2013, 135: 5529
- 10 You, J., Dou, L., Yoshimura, K., Kato, T., Ohya, K., Moriarty, T., Emery, K., Chen, C.C., Gao, J., Li, G. and Yang, Y., *Nat. Commun.*, 2012, 4: 1446
- 11 He, Z., Zhong, C., Su, S., Xu, M., Wu, H. and Cao, Y., *Nat. Photon.*, 2012, 6: 591
- 12 Hou, J., Chen, H.Y., Zhang, S., Chen, R.I. Yang, Y., Wu, Y. and Li, G., *J. Am. Chem. Soc.*, 2009, 131: 15586
- 13 Hellstrom, S., Zhang, F., Inganäs, O. and Andersson, M.R., *Dalton Trans.*, 2009, 10032
- 14 Zoombelt, A.P., Gilot, J., Wienk, M.M. and Janssen, R.A.J., *Chem. Mater.*, 2009, 21: 1663
- 15 He, Y., Chen, H.Y., Hou, J. and Li, Y., *J. Am. Chem. Soc.*, 2010, 132: 5532
- 16 He, Y., Chen, H.Y., Hou, J. and Li, Y., *J. Am. Chem. Soc.*, 2010, 132: 1377
- 17 Cheng, Y.J., Hsieh, C.H., He, Y., Hsu, C.S. and Li, Y., *J. Am. Chem. Soc.*, 2010, 132: 17381
- 18 Lu, Z., Li, C.H., Du, C., Gong, X. and Bo, Z.S., *Chinese J. Polym. Sci.*, 2013, 31(6): 901
- 19 Lei, T., Wang, J.Y. and Pei, J., *Chem. Mater.*, 2014, 26: 594
- 20 Roncali, J., *Acc. Chem. Res.*, 2009, 42: 1719
- 21 Gevaerts, V.S., Herzig, E.M., Kirkus, M., Hendriks, K.H., Wienk, M.M., Perlich, J., Müller-Buschbaum, P. and Janssen, R.A.J., *Chem. Mater.*, 2014, 26: 916
- 22 Keshtov, M.L., Fu, Y.Y., Xie, Z.Y. and Geng, Y.H., Kochurov, V.S. and Khokhlov, A.R., *Chinese J. Polym. Sci.*, 2014, 32(7): 844
- 23 Qin, R., Jiang, Y., Ma, H., Yang, L., Liu, H. and Chang, F., *J. Appl. Polym. Sci.*, 2013, 129: 2671
- 24 Yang, L., Zhou, H. and You, W., *J. Phys. Chem. C*, 2010, 114: 16793
- 25 Lim, E., Jung, B.J., Lee, J., Shim, H.K., Lee, J.I., Yang, Y.S. and Do, L.M., *Macromolecules*, 2005, 38: 4531
- 26 Blouin, N., Michaud, A., Gendron, D., Wakim, S., Blair, E., Neagu-Plesu, R., Belletête, M., Durocher, G., Tao, Y. and Leclerc, M., *J. Am. Chem. Soc.*, 2008, 130: 732
- 27 Aïch, R.B., Blouin, N., Bouchard, A. and Leclerc, M., *Chem. Mater.*, 2009, 21: 751

- 28 Allard, N., Aïch, R.B., Gendron, D., Boudreault, P.L.T., Tessier, C., Alem, S., Tse, S.C., Tao, Y. and Leclerc, M., *Macromolecules*, 2010, 43: 2328
- 29 Dennler, G., Scharber, M.C. and Brabec, C.J., *Adv. Mater.*, 2009, 21: 1323
- 30 Huo, L., Zhang, S., Guo, X., Xu, F., Li, Y. and Hou, J., *Angew. Chem. Int. Ed.*, 2011, 50: 9697
- 31 Piliago, C., Holcombe, T.W., Douglas, J.D., Woo, C.H., Beaujuge, P.M. and Fréchet, J.M.J., *J. Am. Chem. Soc.*, 2010, 132: 7595
- 32 Li, W., Zhou, Y., Viktor Andersson, B., Mattias Andersson, L., Thomann, Y., Veit, C., Tvingstedt, K., Qin, R., Bo, Z., Inganäs, O., Würfel, U. and Zhang, F., *Org. Electron.*, 2011, 12: 1544
- 33 Blom, P.W.M., Mihailetschi, V.D., Koster, L.J.A. and Markov, D.E., *Adv. Mater.*, 2007, 19: 1551
- 34 Ding, P., Zhong, C., Zou, Y., Pan, C., Wu, H. and Cao, Y., *J. Phys. Chem. C*, 2011, 115: 16211
- 35 Li, W., Hendriks, K.H., Furlan, A., Roelofs, W.S.C., Wienk, M.M. and Janssen, R.A.J., *J. Am. Chem. Soc.*, 2013, 135: 18942
- 36 Lei, T., Wang, J.Y. and Pei, J., *Acc. Chem. Res.*, 2014, 47(4): 1117