

X-Shaped Oligothiophenes as a New Class of Electron Donors for Bulk-Heterojunction Solar Cells

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Four X-shaped oligothiophenes with different conjugation length were investigated as novel electron donors in single-layer bulk-heterojunction solar cells. The UV–vis absorption spectra of blends of compounds **1–4** with 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁ show a remarkably red shift and broadening with increasing thiophene number at each of the four branches. The performance of the photovoltaic cells varied significantly with molecular structures of the four oligothiophenes. Conversion efficiencies increased from 0.008% to 0.8% with changing the electron donors from **1** to **4**. The maximum incident photon-to-current conversion efficiency of the device based on **4** reaches 31.6%, much higher than those of three other compounds **1–3**. Remarkable improvement of the device performance was achieved with increasing the substituted thiophene number. The results show that the photovoltaic effect is dependent on the structural characteristics and the film forming abilities of the X-shaped thiophenes.

Introduction

Organic photovoltaic (PV) cells have evolved as a promising cost-effective alternative to silicon-based solar cells, due to their cheap fabrication, easy processing, compatibility with flexible substrates, and low processing temperature.^{1–6} Many efforts have been expended in novel materials synthesis and application in PV devices.⁷ However, energy conversion efficiency is not high enough for commercial application.⁸ The efficiencies of organic PV cells acquired a significant improvement due to introduction of the so-called bulk-heterojunction concept,⁹ where a photoactive layer routinely consists of an interpenetrating network of π -conjugated polymer donors and soluble fullerene acceptors. In this case, the surface area of the donor–acceptor interface has been increased greatly, and excitons experience dissociation wherever they are created within the bulk, thus potentially leading to a high efficiency.¹⁰ A 100% quantum yield for electron transfer at the polymer donor and fullerene acceptor interfaces was observed.^{2,11} On the basis of the polymer–fullerene systems, the power conversion efficiency up to 5.0% has been reported with nanoscale control of the interpenetrating network morphology,¹² and the fill factor also can reach above 67% by self-organization of polymer blends.¹³ This concept has also been applied in organic small molecular PV cells.¹⁴

In recent years, the study of monodisperse well-defined π -conjugated oligomers has achieved its strong field because the developments of new synthetic strategies give us great opportunities to design and synthesize novel π -conjugated oligomeric materials with precise length and constitution.¹⁵ The π -conjugated oligothiophenes have been some of the most promising candidates owing to their excellent electronic proper-

ties with environmental and thermal stabilities, and easy tuning of the properties by introducing functional substituents.¹⁶ A number of substituted derivatives have been synthesized and investigated for organic PV devices.¹⁷ However, most of them have a linear molecular structure, which tends to aggregate because of π – π stacking interactions. Moreover, their photo-physical properties and solubility could not be tuned independently, which is a disadvantage for comprehensive optimization on structures of these materials. Star-shaped compounds combined with conjugated characters of the central core and the three branches would exhibit intrinsic electrical, optical, and morphological properties.¹⁸ The highly branched chemical structures reduce intermolecular interaction and improve the physical properties in the solid state. Currently, C₃-substituted conjugated architectures have attracted increasing attention as possible alternatives to linear oligomers in optoelectronic applications.^{19,20} But few papers have reported on the C₃-symmetric oligothiophene derivatives and their use in the field of PV cells.²⁰ To the best of our knowledge, there is still no report on the investigation of the photovoltaic properties of C₄-substituted oligomers based on the *all*-thiophene units, since the tetrasubstituted thiophenyl precursors are difficult to synthesize.

Here, four X-shaped oligothiophenes are investigated as the novel electron donors for the single-layer bulk-heterojunction photovoltaic cells. The X-shaped oligomers were a novel type of C₄-substituted molecular materials, in which four linear benzenes or oligothiophenes are connected to a thiophene central core by α – α and α – β linkages. The synthesis and characterization of compounds **1–4** have been published elsewhere.²¹ The optical, electrochemical, and photovoltaic properties of the oligothiophenes are compared. The performances of photovoltaic cells exhibit a significant difference with the four oligomers as donors and the soluble 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁ (PCBM) as acceptor, respectively. Remarkable im-

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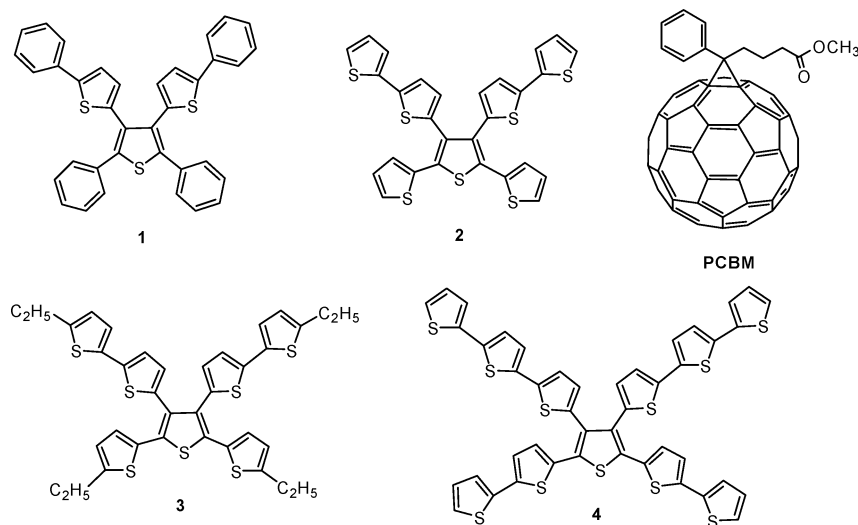


Figure 1. Chemical structures of the four X-shaped oligothiophenes (**1–4**) and PCBM.

provement of the photovoltaic performances was achieved by increasing the number of the substituted thiophene groups. Furthermore, the relationship between the molecular structures of the X-shaped donors and the photovoltaic effect is discussed.

Experimental Section

Materials and Measurements. The synthesis and characterization of novel X-shaped oligothiophene derivatives already have been described elsewhere.²¹ PCBM was synthesized according to the literature.²² Analytical grade *o*-dichlorobenzene was distilled after dehydration according to conventional methods. The UV–vis absorption spectra were measured with a Shimadzu UV-3100 Spectrometer.

Fabrication and Photovoltaic Measurements of the Solar Cells. The single-layer bulk-heterojunction solar cells with a configuration of anode/PCBM-doped oligothiophenes/cathode were fabricated. The ITO-coated glass substrates, used as the transparent anode, were cleaned by conventional methods. Then, the pre-cleaned ITO glass was spin-coated with poly(ethylene dioxythiophene):poly(styrenesulfonic acid) (PEDOT/PSS, Bayer PVP 4083), and dried in a vacuum oven at 120 °C for 10 min. The active layers were built by spin-coating solutions of the blend of the four X-shaped oligothiophenes with PCBM (1:1.2, w/w), respectively. The concentration of the solution was 5 mg mL⁻¹ in *o*-dichlorobenzene. The Al layer was vacuum deposited on the organic layer through a mask under 4×10^{-4} Pa. Current–voltage characteristics of the photovoltaic devices in the dark and under illumination with 100 mW cm⁻² were measured on a computer-controlled Keithley SourceMeter 2400 source measurement system. Illumination was provided by white light from a xenon lamp (Jobin Yvon, FL-1039). Photocurrent was measured with monochromatic light from the xenon lamp and detected by computer-controlled Stanford SR830 Lock-in Amplifier. All the measurements were performed under ambient atmosphere at room temperature.

Results and Discussion

Photophysical and Electrochemical Properties. The molecular structures of the four compounds are shown in Figure 1. The replacement of the linear structure of the oligothiophenes by four branches could increase molecular nonplanar structures and prevent aggregation, so their physical properties in the solid state could be improved greatly. Moreover, these oligomeric

materials have good solubility and excellent thermal stability, so they could be used as the active layer of film devices simply by solution-processing techniques.

Figure 2 shows UV–vis absorption spectra for compounds **1–4** (dot line), PCBM (dash line), and their blends (1:1.2, w/w; solid line) in spin-coated films. Compounds **1–4** all exhibit one peak centered at 312, 337, 341, and 390 nm, respectively. By changing the four branches stepwise, their absorption peaks are progressively red-shifted about 80 nm (from **1** to **4**) due to the increase of conjugation length, and the absorption spectra show obvious broadening (see the dotted lines in Figure 2). Compound **4** especially exhibits a broad absorption peak with a obvious broadening spectrum. In a photovoltaic device, the spectral peculiarities would increase light-harvesting efficiency relative to the other three ones, since the maximum of the solar photon flux is around the red or infrared section.^{3,23}

In this study, we chose the blends of compounds **1–4** with PCBM (1:1.2 w/w) as the active layer of photovoltaic cells. The UV–vis absorption spectra of the four blends in spin-coated films were shown by solid lines in Figure 2. The absorption spectra of the blends show noticeable differences from those of the two parent molecules. The blends show the main absorption peaks at about 266 and 340 nm, and a long tail extending over the whole visible range (from 300 to 600 nm). The second absorption peaks of the blend films turned broader and the tails extend longer with changing structures of the branches and increasing the number of thiophene rings at each of the four branches. In principle, a universal viewpoint for improving the photovoltaic efficiency is the selection and development of new molecules having good overlap of the absorption spectrum with the solar emission spectrum.²⁴ In addition, it is noted that the four absorption spectra of the composites are just a superposition of the peaks of donor compounds and acceptor PCBM without any indication of extra spectral features (see Figure 2). To discuss this result in detail, we used compounds **3** and **4** as examples. Parts c and d of Figure 2 show the absorption spectra of PCBM, compound **3** or **4**, and their blends in solid films. There are two peaks centered at about 266 and 339 nm for PCBM, and only one peak centered at about 390 nm for compound **4**. The blend of compound **4** and PCBM shows three absorption peaks centered at about 266, 339 and 389 nm, which are obviously corresponding to the acceptor PCBM and the donor moiety, respectively. The blend of compound **3** and PCBM shows only two peaks centered at 266

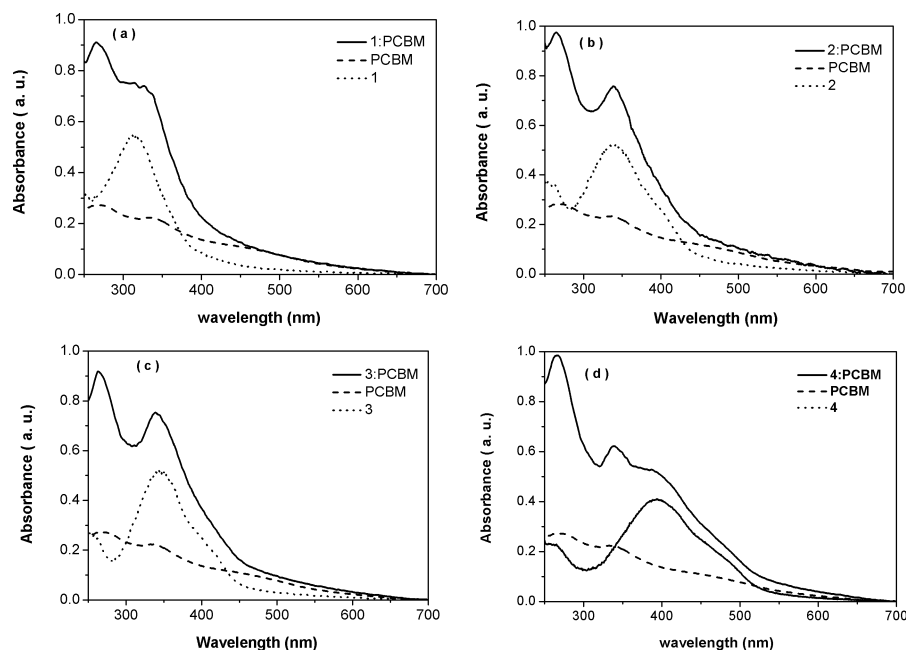


Figure 2. UV-vis absorption spectra for compound **1–4** (dot line), PCBM (dash line), and their blends (1:1.2, w/w; solid line) in spin-coating films.

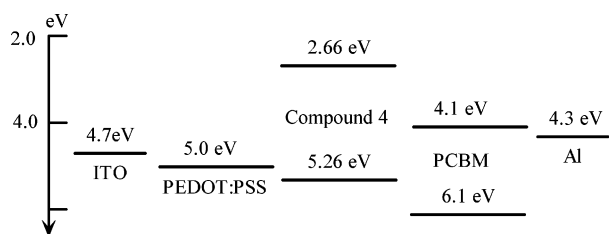


Figure 3. Proposed energy level diagrams for the bulk-junction devices (compound **4** as an example).

and 339 nm, because the absorption peak of compound **3** is at the same position with the second peak of PCBM. These results adequately indicate that there are no significant interactions between the two materials of the blends in the ground state.

A similar effect has also been found in their electrochemical properties by changing the four branches (shown in ref 21). The HOMO levels of four compounds slightly increase from -5.57 to -5.26 eV, while their LUMO levels decrease from -2.18 to -2.79 eV with increasing the thiophene number in the branches. In the device, photoexcited excitons are expected to dissociate at the donor/acceptor interfaces so that negative carriers could be injected into the PCBM and positive ones into the oligothiophene donors. The proposed energy-level diagram of a device provides further insight into the roles of functional materials in the device (Figure 3). The energy level values of the PCBM, PEDOT:PSS, and electrode materials are taken from the literature.¹⁰ Their HOMO levels are all distributed between 5.0 (HOMO of PEDOT:PSS) and 6.1 eV (HOMO of PCBM), and their LUMO levels are higher than 4.1 eV (LUMO of PCBM). The energy-level offset for the donor-acceptor junction is perfect for photoexcited exciton dissociation.²⁵ The energy levels between the donors and PCBM would help by creating exciton charged pairs. Therefore, the photocurrents of PV cells would be increased, and the efficiency of the device also could be improved drastically. In addition, their band gaps turned narrower accordingly with varying the branches (from 3.3 to 2.6 eV). Currently, one obvious route to increase the photovoltaic conversion efficiency is to chemically narrow the band gap of materials.²⁶

Photovoltaic Behavior. Organic bulk-heterojunction photovoltaic cells were fabricated by using compounds **1–4** as electron donors and PCBM as an electron acceptor, which is described in the Experimental Section. We have prepared composite single-layer photodiodes with a structure ITO/PEDOT:PSS/compounds **1–4** + PCBM (1:1.2 w/w)/Al by spin-coating. Under white light illumination at 100 mW cm^{-2} , through the ITO electrode, the photovoltaic cells showed marked photocurrents. Figure 4 shows the typical current-voltage characteristics of the photovoltaic cells. Between -1.0 and $+1.0$ V, all the logarithmically plotted dark currents are rather symmetric to the 0 V center for positive and negative applied voltage. Such symmetry can be explained by the contribution of a small shunt resistivity to the photocurrent, which manifests as “ohmic” behavior in the low current region of a diode.²⁷ Under dark condition, the four I - V curves reveal rectifying semiconductor diode characteristics, especially for the device based on a compound with a rectification rate of 10 at ± 1.5 V (shown in Figure 4d). From the I - V curves, an open circuit voltage (V_{oc}) and a short circuit current (I_{sc}) have been measured. By using these data, a filling factor (FF) and power conversion efficiency were calculated. The solar cell parameters have been summarized in Table 1.

Clearly both short circuit current and open circuit voltage of the four devices are highly dependent on the oligothiophene chain lengths. With an increase in the thiophene units in the four branches, the photovoltaic effects of the oligothiophene donors increase progressively. A short circuit current is 0.12 mA cm^{-2} for compound **1** and 0.29 mA cm^{-2} for compound **2**. For compound **3**, the short circuit current is 1.14 mA cm^{-2} , which is 1 order of magnitude higher than that of the device based on compounds **1** and **2**. It is worthy noting that the short circuit current of the device based on compound **4** reaches 3.65 mA cm^{-2} , higher than those of other oligothiophene/ C_{60} blends.^{17b,20,28} The systematic increase of the photocurrent with the chain extension of the oligothiophene is consistent with the observation that the electron transfer of the compound containing a longer oligothiophene occurs more efficiently, because the lower oxidation potential of the long oligothiophene is more effective for lowering the energy level of the charge-separated

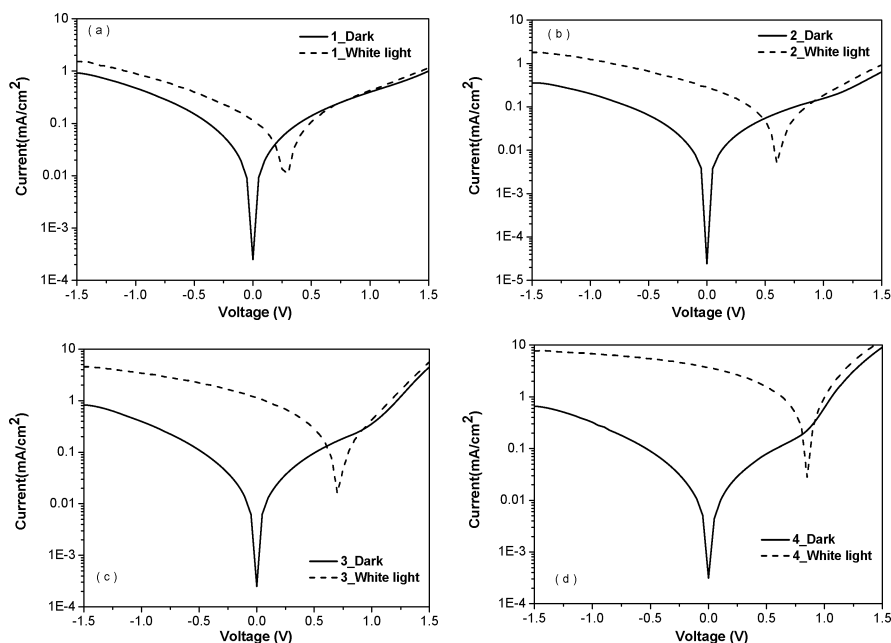


Figure 4. Logarithmic representations of the current density–voltage characteristics of the bulk-heterojunction photovoltaic cells under white light illumination (dash line) and in the dark (solid line).

TABLE 1: Photovoltaic Data for the Materials Studied

blended materials (1:1.2, w/w)	I_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	η_e (%)
1: PCBM	0.12	0.3	0.23	0.0084
2: PCBM	0.29	0.6	0.23	0.04
3: PCBM	1.14	0.7	0.23	0.18
4: PCBM	3.65	0.85	0.26	0.80

state.^{28,29} In contrast to the short circuit current, open circuit voltage appears to experience a slight increase among the four devices (from 0.3 to 0.85 V). Actually, open circuit voltage is due to the splitting of the respective pseudo-Fermi level of electrons and holes, which are represented by the HOMO of the donor and the LUMO of the acceptor, respectively.³⁰ In other words, the V_{oc} should decrease as the donor HOMO increases. Surprisingly, the open circuit voltages obviously increase with the donor HOMO increase (from -5.57 to -5.26 eV). The conflict here indicates some special mechanism or factor for this bulk-heterojunction cell in this study.

It is widely known that photovoltaic properties of photovoltaic cells are greatly affected by the morphology of the thin solid film. To discuss this unusual result, we investigated the morphology of these oligothiophene–PCBM-blend films by atomic force microscopy (AFM). The four pictures have been shown in Figure 5. The results obviously show us that the film-forming abilities of the four compounds with PCBM are very different. Under an optical microscope, the blend films containing compound **1** or **2** with PCBM were not continuous, which indicated that their capabilities of film forming were not good. Though the compatibility of compound **2** and PCBM was improved, there were still larger scale crystals (as shown in Figure 5b), which suggested demixing of compound **2** and PCBM on a very large scale. The blend films of compound **3** and **4** with PCBM were relatively continuous, which indicated the film-forming abilities were better. Comparing the AFM image of blended films containing compound **3** and compound **4** (as shown in Figure 5c,d), the film morphology of blend films containing compound **4** was really smoother and the size of phase separation was smaller, which was better for the PV properties of devices. These pictures show that the film-forming

abilities obviously improve as the donor increases the length of the four branches. Therefore, the improvements of PV properties could be obtained with excellent film-forming abilities. These results are consistent with the PV properties of devices based on the four oligomers as donors in this study. Though compounds **2** and **3** have similar chemical structures, the I_{sc} of the device with compound **3** as donor was about 3 times higher than that with compound **2** as the donor, which would originate from improvement of the film-forming ability by ethyl substituents. When the electron donors changed from compound **1** to **4**, the open circuit voltages obviously improve, and their power conversion efficiencies of PV devices increase 2 orders of magnitude (from 0.008% to 0.8%).

The spectra of photocurrent action and incident photon-to-current conversion efficiency (IPCE) were also measured. The normalized photocurrent action spectra of the bulk-heterojunction photovoltaic cells are shown in Figure 6. With an increase in the number of thiophene rings and conjugation length of the donors, the photocurrent response range of the blends turned broader in visible light. The larger overlap of the photocurrent spectrum based on compound **4** with the solar emission spectrum resulted in an increase of light-harvesting efficiency relative to three other donors. Figure 7 shows the spectra of monochromatic IPCE. The IPCE is calculated from the spectrally resolved short-circuit current by the following equation:

$$\text{IPCE} (\%) = \frac{1240 \times I_{sc} (\mu\text{A} \cdot \text{cm}^{-2})}{\lambda (\text{nm}) \times P_{in} (\mu\text{W} \cdot \text{cm}^{-2})} \times 100\% \quad (1)$$

where P_{in} is the intensity of the incident light.

The onset wavelengths of the IPCE spectra for the devices based on compounds **1–4** were about 550, 600, 630, and 665 nm, respectively. There is a big difference in the values of IPCE among the four devices based on different donors. The maximum IPCEs of the devices are about 2.3%, 4.2%, and 16.0% for compounds **1–3**, respectively. However, the IPCE values of a device based on compound **4** were found higher than 25% in the 350–465 nm range with a maximum of 31.6% at 400 nm, which is much higher than those of the three other

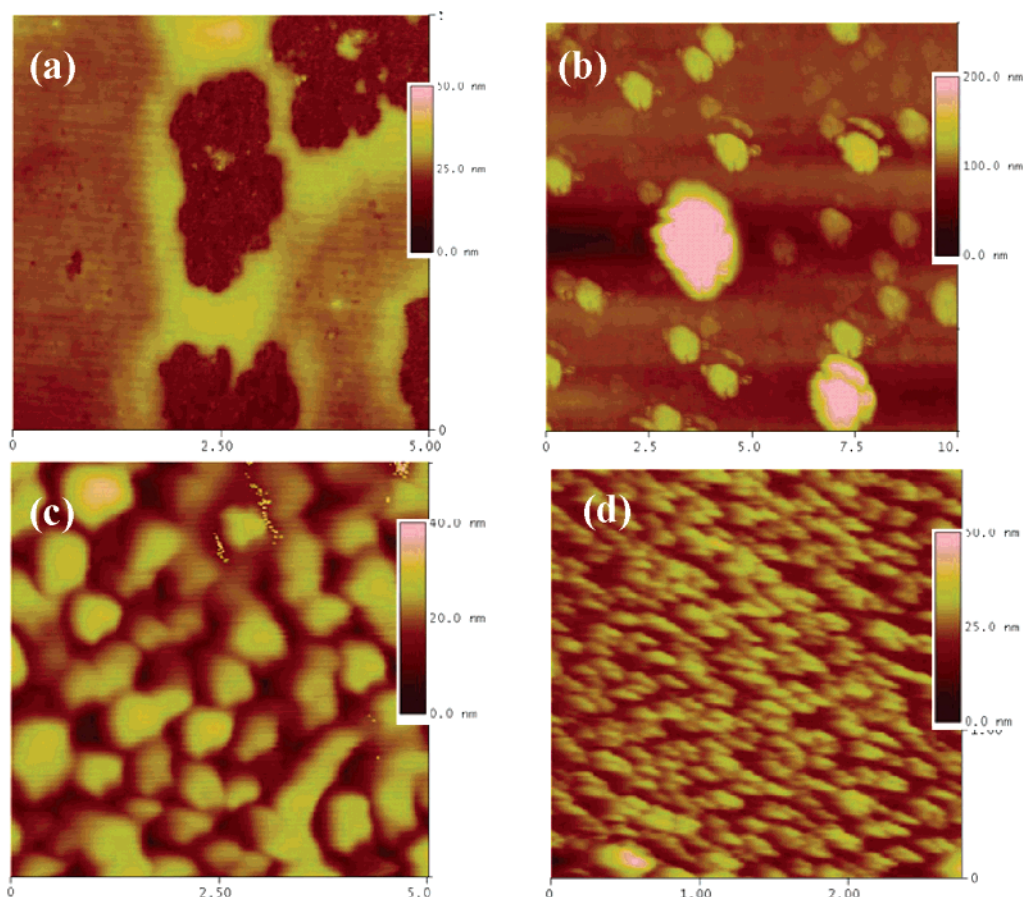


Figure 5. AFM images showing the surface morphology of (a) PCBM/1, (b) PCBM/2, (c) PCBM/3, and (d) PCBM/4 composite films spin-coated from *o*-dichlorobenzene solution.

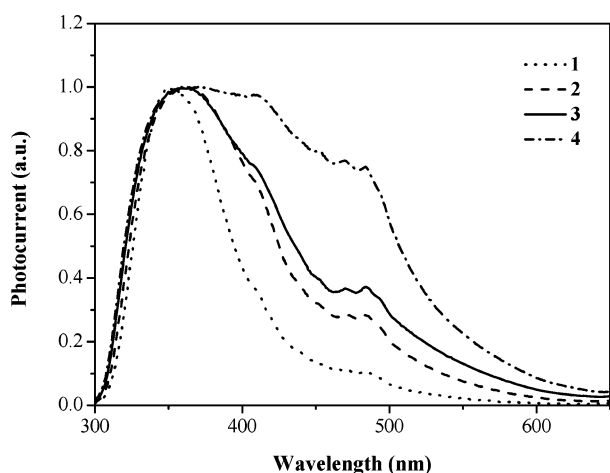


Figure 6. Normalized photocurrent action spectra of the bulk-heterojunction photovoltaic cells irradiated with 100 mW cm^{-2} .

compounds. The much higher photocurrent and IPCE value of the device with compound **4** as donor indicates a more efficient charge creation, separation, and transport within the donor–PCBM-blend film, which would originate from better film forming ability and smaller band gap between the HOMO of **4** and LUMO of PCBM.

The film morphology and IPCE studies for bulk-heterojunction PV devices with different donors indicate that the photovoltaic conversion efficiency is strongly related to the molecular structures of the donors. The electrochemical and photo-physical properties of the four oligomers are quite different with increasing number of thiophene rings at each of the four

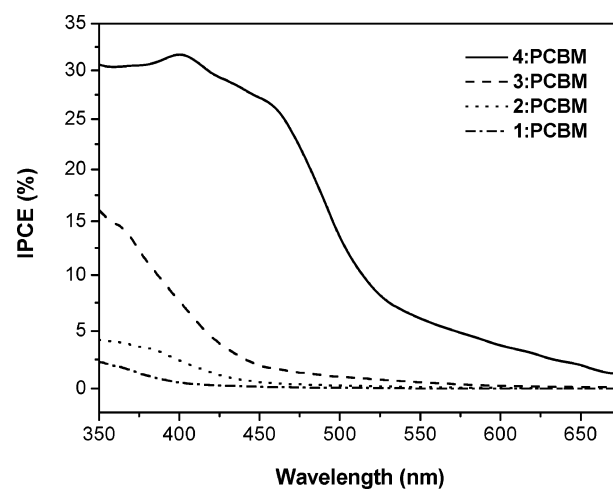


Figure 7. Spectra of monochromatic IPCE for the bulk-heterojunction photovoltaic cells.

branches. The red shift and broadening of the absorption spectrum of the blend with compound **4** increase the light-harvesting efficiency relative to the three other donors, and result in obvious improvement of photovoltaic performance. These preliminary results are better than or comparable with those of single-layer bulk-heterojunction photovoltaic cells reported.^{11a,17b,c,28,31} The photovoltaic characteristics can be further improved by changing the layer thickness of the organic layer and treating the device with heat etc. The structure modifications of these X-shaped donors and further study on the structure–property relationship are in progress.

Conclusion

In conclusion, the simple organic single-layer bulk-heterojunction photovoltaic cells with four X-shaped oligothiophenes as novel donors and PCBM as an acceptor were fabricated. By increasing the number of thiophene rings at each of the four branches, the absorption spectra of the four compounds red-shift and broaden, light-harvesting efficiency increases, and the photovoltaic performance improves. Conversion efficiencies vary from 0.008% to 0.8% by changing the electron donors from compound **1** to **4**. The much higher photocurrent and IPCE value of the device with compound **4** as donor indicates a more efficient charge creation, separation, and transport within the donor–PCBM-blend film, which would originate from the better film forming ability and the smaller band gap between the HOMO of **4** and LUMO of PCBM. Therefore, these promising preliminary results provide a great impetus to developing the molecular engineering of organic semiconductors for increasing the photovoltaic cell efficiency.

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