Tuning Surface Energy of Conjugated Polymers via Fluorine Substitution of Side Alkyl Chains: Influence on Phase Separation of Thin Films and Performance of Polymer Solar Cells

Yanfeng Liu,1,8 Dandan Tang,2,8 Kaicheng Zhang,† Peng Huang,† Zhaowei Wang,† Kai Zhu,† Zhendong Li,† Ligang Yuan,† Jian Fan,‡* Yi Zhou,§* and Bo Song‡,*†

†College of Chemistry, Chemical Engineering and Materials Science, and ‡Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), and Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, China

ABSTRACT: Different contents of fluorine in side alkyl chains were incorporated into three conjugated polymers (namely, PBDTTT-f13, PBDTTT-f9, and PBDTTT-f5) whose backbones consist of benzodithiophene donors and thienothiophene acceptors. These three fluorinated polymers, in comparison with the well-known analogue PTB7-Th, show comparable energy levels and optical band gaps. However, the fluorination of side alkyl chains significantly changed the surface energy of bulk materials, which leads to distinctly different self-assembly behaviors and phase separations as being mixed with PC71BM. The increased mismatch in surface energies between the polymer and PC71BM causes larger scale phase domains, which makes a sound explanation for the differences in their photovoltaic properties.

INTRODUCTION

A significant progress in bulk heterojunction (BHJ) polymer solar cells (PSCs) has been achieved through developments in both novel molecular design and optimized device architectures.1−4 As a result, the performance of BHJ-PSCs has exceeded 11% in power conversion efficiency (PCE).5,6 In most of the cases, the active layer of BHJ-PSCs is a blend of electron-rich polymers as a donor and electron-deficient fullerene derivatives as an acceptor to form an interpenetrating nanoscopic network. For typical conjugated polymers, the exciton diffusion length is rather short, usually on the order of tens of nanometers. If the phase domains are bigger than the diffusion length, the recombination possibility of excitons will dramatically increase.7,8 Therefore, a well-defined phase separation with appropriate domain size is critical to efficient charge dissociation and also centrally important for providing the continuous percolation pathway for smooth charge transport with minimized charge losses.

To optimize the phase separation of a photoactive layer, many efforts have been focused on manipulating device-processing conditions, including blend ratio,9,10 thermal/solvent annealing,11−13 and introduction of additives.14,15 Beyond the conditional control, the nature of the materials determined by their molecular structures is more decisive to the phase segregation of BHJ blend films.16,17 In this regard, a compromise is often made between the polymer donor and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) acceptors. That is, a good phase separation demands a difference between their surface energies, that is, an immiscible nature, whereas a great difference is not favorable for the formation of uniform phase separation.18,19 In this regard, surface energy was first introduced to explain the phase separation phenomenon by Kim et al. in 2010.20 They found that the terminal groups of the P3HT polymer have great influence on the surface energy, similar to the surface morphology of P3HT/PCBM blend films. Following this strategy, Sun et al.21 were able to tune the surface morphology of BHJ thin films by controlling the content of cyanohexane side chains in conjugated polymers. They all observed that highly miscible blends with nanoscale phase separation could be achieved when two components of an active layer had a similar surface energy, whereas polymers with large surface energy differences to PCBM tend to result in a large domain size and a significant phase separation.

In recent years, fluorinated conjugated materials have been widely used in organic photovoltaics.22 Fluorine atoms, because of their strong electron-withdrawing effect, would lower both the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level.23−26 In addition, this modification is in favor of higher photoelectron conversion as being applied in BHJ-PSCs.27−30 Compared with the nonfluorinated counterparts, fluorinated polymers exhibit a series of unique features such as high thermal stability,
enhanced chemical resistance, and low surface energy.\textsuperscript{31} Given the phase separation of the blend films, whether the lowered surface energy is a positive or negative factor calls for an answer. According to our knowledge, there is no precedent work that systematically investigates the role of a fluorinated side alkyl chain acting in surface energy as well as the phase separation in BHJ blend films.

Herein, a series of conjugated polymers based on alternating benzodithiophene (BDT) units as an electron donor and thienothiophene (TT) units as an electron acceptor were synthesized, named PBDTTT-f\textsubscript{x} \textbf{(x = 13, 9, 5)} series polymers, where \textit{x} stands for the number of fluorine atoms in the side chain of TT unit. The molecular structures of these polymers are presented in Scheme 1. The energy levels and photo-absorption abilities of fluorinated polymers are similar to those of their known counterpart PTB7-Th.\textsuperscript{32} As being applied as donors in BHJ-PSCs, quite different device performances were obtained. The surface morphology analysis indicates that a well-defined phase separation of the BHJ blend film corresponds to higher device performance. The phase separation, we believe, should be correlated with the surface energy of individual polymers that are deduced from the results of a group of contact angle measurements. The surface energies of PBDTTT-f13, PBDTTT-f9, PBDTTT-f5, and PTB7-Th are 19.6, 22.3, 25.8, and 32.0 mJ/m\textsuperscript{2}, respectively. As for the acceptor material, PC\textsubscript{71}BM owns a surface energy of 31.0 mJ/m\textsuperscript{2}. A high-quality phase separation and a high device performance were achieved as PTB7-Th:PC\textsubscript{71}BM pair was applied as the photoactive materials. This work gives us a hint that the surface energy of the targeting materials should be taken into account as designing new polymer donors.

Scheme 1. Synthetic Route and Molecular Structures of PBDTTT-f13, PBDTTT-f9, and PBDTTT-f5
RESULTS AND DISCUSSION

Ultraviolet–visible (UV–vis) spectra of PBDTTT-fx-based polymers in chloroform and in the film state are shown in Figure 1. The absorption peaks of PBDTTT-f13, PBDTTT-f9, and PTB7-Th are similar, whereas the absorption peak of PBDTTT-f5 shows a blue shift compared with those of others. The former three polymers exhibited an intense absorption from 500 to 800 nm with two peaks at around 650 and 700 nm, which can be ascribed to the intramolecular charge transfer and interchain interaction, respectively.33,34 To understand the blue shift of PBDTTT-f5, polymer solutions were heated from 30 to 100 °C. As shown in Figure 2, the absorption spectra indicate a temperature-dependent feature. For all polymers, the peak at around 700 nm decreased with the increase in temperature and shifted to short wavelength. An extreme case is that the corresponding peak of PBDTTT-f5 almost disappeared as the temperature was elevated to 100 °C. Knowing the fact that the peak at around 700 nm corresponds to the interchain interactions of the polymers, it can be concluded that the intermolecular interaction between PBDTTT-f5 should be less stronger than the rest of the polymers.

The LUMO energy levels \( E_{\text{LUMO}} \) of PBDTTT-f13, PBDTTT-f9, PBDTTT-f5, and PTB7-Th were determined by cyclic voltammetry (CV), as shown in Figure 3. The onset reduction potentials \( E_{\text{red}} \) of PBDTTT-f13, PBDTTT-f9, PBDTTT-f5, and PTB7-Th were 1.31, 1.32, 1.34, and 1.39 V, respectively. \( E_{\text{LUMO}} \) of these polymers can be calculated using the equation \( E_{\text{LUMO}} = - (E_{\text{red}} + 4.80) \) (eV). Therefore, the \( E_{\text{LUMO}} \) values of PBDTTT-f13, PBDTTT-f9, PBDTTT-f5, and PTB7-Th are −3.49, −3.48, −3.46, and −3.41 eV, respectively. The HOMO energy levels \( E_{\text{HOMO}} \) can be calculated according to the equation \( E_{\text{HOMO}} = E_{\text{LUMO}} + E_{\text{opt}} \). All band gaps and energy levels are summarized in Table 1. The PBDTTT-fx series polymers show comparable energy levels with those of PTB7-Th, indicating that fluorination of the side chain has little effect on the energy levels of the polymers.

The surface morphologies of the as spin-coated films were observed using atomic force microscopy (AFM), as shown in Figure 4. The PBDTTT-fx series polymers, except for...
PBDTTT-f5, showed surface topologies similar to those of PTB7-Th. Interdigitated fibrous nanostructures with a width of around 10 nm were observed in all polymer films. Because the number of fluorine atoms is small, for example, PBDTTT-f5, the relatively ordered self-assembled nanostructures are formed in comparison with PTB7-Th. These results are consistent with the conclusion drawn by Cho et al.\(^3\)\(^5\) that the interactions of fluorine can strengthen the interactions between the side alkyl chains. Further increasing the fluorine atoms should enhance this effect. Therefore, for PBDTTT-f13 and PBDTTT-f9, interdigitated fibrous nanostructures were observed in the films as well.

To investigate the miscibility of PBDTTT-f\(_x\) series polymers and PC\(_{71}\)BM in blend films, AFM investigation on PBDTTT-f\(_x\):PC\(_{71}\)BM and PTB7-Th:PC\(_{71}\)BM blend films was performed. In Figure 4, all polymers revealed similar surface profiles. However, drastic differences between the surface morphologies of the blends were observed, as shown in Figure 5. In Figure 5a, the PBDTTT-f13:PC\(_{71}\)BM blend shows the formation of large, isolated aggregates, and the domain sizes are more than hundreds of nanometers. This morphology is probably due to the low entropy of mixing between the polymer and PC\(_{71}\)BM because immiscible materials tend to phase-segregate into large domains during the spin-coating process. Considering the relatively short diffusion length of excitons, which is usually less than 10 nm, these large phase domains are disadvantageous for efficient exciton dissociation in the BHJ films. With a lower content of fluorine atoms, as shown in Figure 5b, the spherical domains did not exist in the morphology of the PBDTTT-f9:PC\(_{71}\)BM blend, whereas some distinct aggregates still exist. On the other hand, the blend films of PBDTTT-f5:PC\(_{71}\)BM show a favorable interpenetrating network in Figure 5c, which are similar to the morphology of PTB7-Th:PC\(_{71}\)BM blends shown in Figure 5d. Besides, the PTB7-Th:PC\(_{71}\)BM blend films show smoother surface [with a root-mean-square (rms) roughness of 1.4 nm] than PBDTTT-fx:PC\(_{71}\)BM blend films (the rms roughness values of PBDTTT-f5:PC\(_{71}\)BM, PBDTTT-f9:PC\(_{71}\)BM, PBDTTT-f13:PC\(_{71}\)BM, and PTB7-Th:PC\(_{71}\)BM were 1:1.5 for PBDTTT-fx and PTB7-Th).

### Table 1. Absorption Peaks (\(\lambda\)), Optical Band Gaps (\(E_{\text{g,opt}}\)), and Energy Levels of the Polymers

| polymer   | \(\lambda\) (nm) | \(E_{\text{g,opt}}\)^a (eV) | LUMO\(^b\) (eV) | HOMO\(^c\) (eV) |
|-----------|------------------|------------------------------|-----------------|-----------------|
| PBDTTT-f13| 635, 696         | 1.59                         | −3.49           | −5.08           |
| PBDTTT-f9 | 635, 696         | 1.59                         | −3.48           | −5.08           |
| PBDTTT-f5 | 620, 660         | 1.63                         | −3.46           | −5.09           |
| PTB7-Th   | 638, 701         | 1.61                         | −3.41           | −5.02           |

\(^a\)Calculated from the absorption band edge of the polymers in the film state. \(^b\)Calculated by \(E_{\text{red}}\) from the CV curves. \(^c\)Calculated from the difference between LUMO levels and corresponding \(E_{\text{g,opt}}\).

Figure 4. AFM height images of the spin-coated films of PBDTTT-f13 (a), PBDTTT-f9 (b), PBDTTT-f5 (c), and PTB7-Th (d).

Figure 5. AFM height (top row), adhesion (middle row), and TEM (bottom row) images of blend films prepared by the spin coating of PBDTTT-f13:PC\(_{71}\)BM (a,e,i), PBDTTT-f9:PC\(_{71}\)BM (b,f,j), PBDTTT-f5:PC\(_{71}\)BM (c,g,k), and PTB7-Th:PC\(_{71}\)BM (d,h,l). The blend ratios of polymer:PC\(_{71}\)BM were 1:1.5 for PBDTTT-fx and PTB7-Th.
The measurement of surface energy was recorded to clarify the reason for the formation of different morphologies of blend films. The contact angles of the PBDTTT-fx series polymers, PTB7-Th, and PC71BM were measured using liquid drops of water ($\theta_{\text{water}}$) and monoethylene glycol (MEG) ($\theta_{\text{MEG}}$), as shown in Table 2. The surface energies ($\gamma_{SV}$) were calculated by the following equation.\[\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p\]

where $\theta$ is the contact angle of a liquid drop on the surface of the samples and $\gamma_{LV}$, $\gamma_{SV}^d$, and $\gamma_{SV}^p$ correspond to the surface energy of water and MEG, dispersive component, and polar component of the surface energy of water and MEG, respectively.

The photovoltaic properties of these polymers were investigated in PSCs with a conventional device configuration: ITO/PEDOT:PSS ($\sim$40 nm)/polymer:PC71BM/Ca ($\sim$20 nm)/Al ($\sim$80 nm). The performance of the PSCs was investigated by recording the respective current density–voltage ($J-V$) curves and external quantum efficiency (EQE) curves, as shown in Figure 6. Detailed parameters including open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor (FF), and PCE are summarized in Table 4. The $J_{sc}$ values of PC71BM, and PBDTTT-f13:PC71BM blends were 1.7, 2.1, and 3.3 nm, respectively). This well-tuned morphology is beneficial to efficient exciton dissociation and charge transportation. Because immiscibility in a donor/acceptor blend arises from the large surface energy difference between the donor and acceptor materials, the homogeneous network of the PBDTTT-f5:PC71BM and PTB7-Th:PC71BM blends can be ascribed to the well-matched surface energies between the donor and the acceptor. For Figure 5i−l, the transmission electron microscopy (TEM) images accord with the AFM results.

The measured surface energy was recorded to clarify the reason for the formation of different morphologies of blend films. The contact angles of the PBDTTT-fx series polymers, PTB7-Th, and PC71BM were measured using liquid drops of water ($\theta_{\text{water}}$) and monoethylene glycol (MEG) ($\theta_{\text{MEG}}$), as shown in Table 2. The surface energies ($\gamma_{SV}$) were calculated by the following equation.

\[
\gamma_{LV}(1 + \cos \theta) = 2 \sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2 \sqrt{\gamma_{SV}^p \gamma_{LV}^p}
\]

\[
\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p
\]

where $\theta$ is the contact angle of a liquid drop on the surface of the samples and $\gamma_{LV}$, $\gamma_{SV}^d$, and $\gamma_{SV}^p$ correspond to the surface energy of water and MEG, dispersive component, and polar component of the surface energy of water and MEG, respectively.

The surface energies of PBDTTT-fx, PTB7-Th, and PC71BM are summarized in Table 3. The increase of fluorine atoms in the BDT side chain led to a lowered surface energy value, 19.6, 22.3, 25.8, and 32.0 mJ/m$^2$ for PBDTTT-f13, PBDTTT-f9, PBDTTT-f5, and PTB7-Th, respectively. The surface energy of PC71BM was also measured to be 31.0 mJ/m$^2$, which is close to that of PTB7-Th. The surface energy differences between donor polymers and the PC71BM acceptor ($\Delta\gamma_{SV}$) decreased consistently from PBDTTT-f13 to PTB7-Th; as a result, an uniform BHJ blend was obtained from the PTB7-Th:PC71BM mixture because of the well-matched surface energies between PTB7-Th and PC71BM. On the basis of the AFM and contact angle results, therefore, better performance is expected from the BHJ solar cells fabricated with a PTB7-Th:PC71BM film as the active layer.

The photovoltaic properties of these polymers were investigated in PSCs with a conventional device configuration: ITO/PEDOT:PSS ($\sim$40 nm)/polymer:PC71BM/Ca ($\sim$20 nm)/Al ($\sim$80 nm). The performance of the PSCs was investigated by recording the respective current density–voltage ($J-V$) curves and external quantum efficiency (EQE) curves, as shown in Figure 6. Detailed parameters including open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor (FF), and PCE are summarized in Table 4. The $J_{sc}$ values...
were all consistent with the integrated photocurrents \(J_{sc}(EQE)\) determined by the EQE spectra in Figure 6b. The photovoltaic device based on the PBDTTT-f13:PC71BM showed the lowest PCE of only 1.98\%, with \(V_{oc}\) of 0.77 V, \(J_{sc}\) of 5.00 mA/cm\(^2\), and FF of 51.2\%. The poor device performance of PBDTTT-f13:PC71BM can be attributed to the large-scale heterogeneities where the domain sizes are too large to achieve efficient exciton dissociation. However, the PTB7-Th:PC71BM device yields the highest PCE of 7.56\%, which is almost 4 times enhanced than that of the PBDTTT-f13:PC71BM solar cell, with an increased \(J_{sc}\) of 14.14 mA/cm\(^2\) and FF of 68.3\%. The result of a significantly enhanced \(J_{sc}\) value showed that the favorable interpenetrating morphology facilitates more efficient charge dissociation and transport in the active layer, which leads to a higher device performance.

The PBDTTT-f9:PC71BM device showed a slightly increased PCE of 2.47\% as compared with PBDTTT-f13:PC71BM, and the BHJ device based on PBDTTT-f5 showed a moderately increased PCE of 5.93\%. The upward trend in PCE from PBDTTT-f13:PC71BM to PTB7-Th:PC71BM devices can be correlated with the well-tuned morphology of the active layer and the well-matched surface energies between donor polymers and the fullerene acceptor.

To gain an insight understanding of the tendency of PCEs, the charge extraction properties were studied by plotting the photocurrent density \(J_{ph}\) versus the effective voltage \(V_{eff}\) of the solar cells. \(J_{ph}\) can be determined by the equation \(J_{ph} = J_{sc} - J_{0}\), where \(J_{sc}\) and \(J_{0}\) are the photocurrent densities under illumination and in the dark, respectively. \(V_{eff}\) can be determined by the equation \(V_{eff} = V_{o} - V_{i}\), where \(V_{o}\) is the voltage at \(J_{ph} = 0\) and \(V\) is the corresponding applied voltage. As shown in Figure 7, \(J_{ph}\) of each device reaches saturation (where

| polymer       | \(V_{oc}\) (V) | \(J_{sc}\) (mA/cm\(^2\)) | FF (%) | PCE_{max} (%) | \(J_{sc}\) (EQE) (mA/cm\(^2\)) |
|---------------|---------------|-------------------|--------|--------------|-------------------------------|
| PBDTTT-f13    | 0.77          | 5.00              | 51.2   | 1.98         | 4.41                          |
| PBDTTT-f9     | 0.75          | 6.05              | 54.7   | 2.47         | 5.24                          |
| PBDTTT-f5     | 0.81          | 11.98             | 61.3   | 5.93         | 11.94                         |
| PTB7-Th       | 0.77          | 14.41             | 68.3   | 7.56         | 14.02                         |

Figure 7. \(J_{ph}-V_{eff}\) curves of the PSCs based on PBDTTT-fx:PC71BM and PTB7-Th:PC71BM.

the corresponding current density is defined as \(J_{sat}\) at high \(V_{eff}\) value, suggesting that all charge carriers generated in the photoactive layers are extracted by the electrodes. \(J_{sat}\) under the maximum power point (where the corresponding current density is defined as \(J_{mp}\)) of each device is calculated from the \(J-V\) curves. \(J_{sat}\) \(J_{mp}\), and the ratio of \(J_{mp}/J_{sat}\) are summarized in Table 5. The ratio of \(J_{mp}/J_{sat}\) for the PSC based on PTB7-Th:PC71BM was 66\%, indicating that more than half of the photogenerated carriers were collected by the electrodes at the maximum power point. The efficient charge collection might be resulted from the well-tuned morphology of the blend films. By contrast, the ratio of \(J_{mp}/J_{sat}\) decreased to 63, 40, and 38\% when PTB7-Th was replaced by PBDTTT-f13, PBDTTT-f9, and PBDTTT-f5, respectively. These results further confirm that a good phase separation should be responsible for the efficient extraction from the active layer to the electrodes.

The charge transport property in the photoactive layers was also investigated using the space-charge-limited current equation to calculate the carrier mobilities. The corresponding \(J-V\) curves (Figures S1 and S2) and detailed data (Tables S1 and S2) are presented in the Supporting Information. For the pristine polymer films, the hole mobilities of the polymers increased with the number of F atoms in the side alkyl chains. These results indicate that increasing F contents in the side alkyl chains can improve the charge transport properties of PBDTTT-fx polymers. However, for the blend films, the hole mobilities showed a reverse trend; that is, they decreased with the number of F atoms in the side alkyl chains, and the electron mobilities also showed a downward trend when increasing the number of F atoms. These results suggest that the charge transportation inside of the active layers will be hindered with an increase in the number of F atoms because of the excessive phase separation in the blend films.

In addition to \(J-V\) and \(J_{ph}-V_{eff}\) characteristics, the alternating current impedance spectrometry (ACIS) of the devices was measured. Figure 8a—d shows the Nyquist plots of the solar cell based on PBDTTT-fx polymers and PTB7-Th blend with PC71BM at the corresponding \(V_{oc}\) bias voltages in the dark. The complete device can be modeled as the three different regions for carrier relaxation. From high to low (i.e., left to right) frequency, the impedance responses correspond to the active layer \((R_{f} \text{ and } C_{f})\), the buffer layer region \((R_{2} \text{ and } C_{2})\), and the interface between the buffer layer and the active layer \((R_{3} \text{ and } C_{3})\). The equivalent circuit shown in Figure 8e was employed to fit the Nyquist plots. The parameters fitted from the ACIS are listed in Table 6. The equivalent circuit is represented as the combination of parallel resistance—capacitance circuits in series. \(R_{f}\) is regarded as the contribution of the series resistance between the two electrodes and the external circuit, which reflects the properties of the conductive electrode and is not addressed in the rest of the discussion. Generally, smaller resistances facilitate the transfer of charge carriers, thus leading to better performance.

For the PSCs using PBDTTT-f13 as a donor, \(R_{f}\) shows the largest value among PBDTTT-fx and PTB7-Th polymers. Owing to the decrease in the amount of fluorine atoms in the alkyl side chain, the value of \(R_{f}\) shows a downward trend from PBDTTT-f13 to PTB7-Th, indicating more efficient exciton transport arising from the formation of an interpenetrating network in the BHJ layer, and this result is in accordance with the AFM image. The downward trend of \(R_{f}\) and \(R_{3}\) from

Table 4. Maxima \(J-V\) Characteristics and Integrated \(J_{sc}\) from the EQE of PSCs Based on Polymer:PC71BM Blends

| polymer       | \(V_{oc}\) (V) | \(J_{sc}\) (mA/cm\(^2\)) | FF (%) | PCE_{max} (%) | \(J_{sc}\) (EQE) (mA/cm\(^2\)) |
|---------------|---------------|-------------------|--------|--------------|-------------------------------|
| PBDTTT-f13    | 0.77          | 5.00              | 51.2   | 1.98         | 4.41                          |
| PBDTTT-f9     | 0.75          | 6.05              | 54.7   | 2.47         | 5.24                          |
| PBDTTT-f5     | 0.81          | 11.98             | 61.3   | 5.93         | 11.94                         |
| PTB7-Th       | 0.77          | 14.41             | 68.3   | 7.56         | 14.02                         |

Table 5. \(J_{sat}\) and \(J_{mp}\) of the PSCs Based on PBDTTT-fx:PC71BM and PTB7-Th:PC71BM

| polymer       | \(J_{sat}\) (mA/cm\(^2\)) | \(J_{mp}\) (mA/cm\(^2\)) | \(J_{mp}/J_{sat}\) (%) |
|---------------|-------------------|-------------------|-------------------|
| PBDTTT-f13    | 5.54              | 2.10              | 38               |
| PBDTTT-f9     | 8.81              | 3.55              | 40               |
| PBDTTT-f5     | 12.88             | 8.06              | 63               |
| PTB7-Th       | 17.17             | 11.36             | 66               |
PBDTTT-f13:PC71BM to PTB7-Th:PC71BM device also indicates the influence of surface morphology on the device performance.

■ CONCLUSIONS

In summary, a series of donor-/acceptor-conjugated polymers bearing different alkyl chains with varying fluorine contents were designed and synthesized. Their surface energies were systematically investigated and applied as a metric for the interpretation of phase separation of the blend films of polymer and PC71BM. Taking the surface energy of PC71BM (31.0 mJ/m²) as a reference, the differences between the polymer and PC71BM are increasing with the fluorine content in the alkyl chains, and consequently, the phase domains of the corresponding films also increased. These variation tendencies make a sound explanation to the device performances when these polymers are applied as donors in PSCs. For PBDTTT-f5 and PTB7-Th whose surface energies were close to that of PC71BM, their blend films showed clear phase boundaries and smaller phase domains of ~40 nm, and the corresponding PSCs achieved higher PCEs in the form of better Jsc and FF. Phase separation of BHJ blend films is one of the most important issues that can greatly affect the device performances. The present research demonstrated that surface energy is one of the key factors that should be taken into account as designing new conjugated polymers for highly efficient PSCs.

■ EXPERIMENTAL SECTION

Materials and Instruments. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol, 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexanol, and 3,3,4,4,4-pentafluoro-1-butanol were purchased from Energy Chemical. 1,6-Dibromohexane, 1,8-dibromooctane, 1,10-dibromoodecane, tetrabutylammonium bromide (TBAB), tetrakis(triphenylphosphine)palladium, tetrabutylammonium hexafluorophosphate (n-Bu4NPF6), trichlorobenzene, o-dichlorobenzene (o-DCB), and pyridine were purchased from J&K Scientific. Oxalyl chloride was purchased from Tokyo Chemical Industry Co., Ltd. Dichloromethane (DCM) and petroleum ether were purchased from Titan Scientific Co., Ltd. Sodium chloride, sodium hydroxide, anhydrous magnesium sulfate, MEG, N,N-dimethylformamide (DMF), N-methyl pyrrolidone (NMP), methanol, hexane, ether, acetone, and isopropanol were purchased from Sinopharm Chemical. All of these chemicals were used without further purification, unless otherwise noted. Toluene, DMF, and DCM were purified by a solvent purification system manufactured by Innovative Technology Ltd. PTB7-Th (Mn = 57.6 kg·mol⁻¹, Mw = 106.7 kg·mol⁻¹, and PDI = 1.85) and PC71BM were purchased from Solamer Materials Inc. ITO glass was obtained from CSG.

Table 6. Detailed Parameters of the Equivalent Circuits for the PSCs Operated in the Dark with Applied Bias Voltages Near Their Corresponding Voc

| polymer    | Rs (Ω) | R1 (Ω) | C1 (nF) | R2 (Ω) | C2 (nF) | R3 (Ω) | C3 (nF) |
|------------|--------|--------|---------|--------|---------|--------|---------|
| PBDTTT-f13 | 61.9   | 308.8  | 8.4     | 9079.0 | 1.9     | 11233.0| 2.4     |
| PBDTTT-f9  | 66.6   | 92.0   | 9.0     | 440.3  | 17.9    | 1399.0 | 3.5     |
| PBDTTT-f5  | 29.6   | 76.7   | 5.7     | 238.5  | 5.2     | 323.9  | 13.2    |
| PTB7-Th    | 51.8   | 32.6   | 14.5    | 57.1   | 27.4    | 172.4  | 5.7     |

Figure 8. (a–d) Nyquist plots of the PSCs based on different polymer:PC71BM blends as the active layers. (e) Equivalent circuit used to fit the Nyquist plots.
Holding Co., Ltd. Ca and Al were acquired from Zhongnuo Advanced Material (Beijing) Technology Co., Ltd.

Contact angle measurements were recorded on a KRÜSS DSA100 surface analysis system. The gel permeation chromatography (GPC) measurement was recorded on an Agilent PL-GPC220 chromatograph at 160 °C with trichlorobenzene as an eluent. 1H NMR spectra were recorded on an Avance III 400 MHz spectrometer produced by Bruker Co. Mass spectra were taken on a Thermo ISQ mass spectrometer using a direct exposure probe. UV−vis spectra were recorded on a Cary 2000 spectrometer produced by Agilent Technologies. CVs of polymers were recorded on a CHI660 voltammetric analyzer at room temperature in a 0.1 M n-Bu4NPF6 solution under nitrogen gas protection. The J−V characteristics were measured using a Keithley 236 Source Measure Unit, under AM 1.5G illumination from a xenon-lamp-based solar simulator (SAN-Electric Co., Ltd.) with an irradiation intensity of 100 mW/cm2. The EQE was measured based solar simulator (SAN-Electric Co., Ltd.) with an Measure Unit, under AM 1.5G illumination from a xenon-lamp-characteristics were measured using a Keithley 236 Source Measure Unit, under AM 1.5G illumination from a xenon-lamp-based solar simulator (SAN-Electric Co., Ltd.) with an irradiation intensity of 100 mW/cm2. The EQE was measured.

**Synthesis of Monomers and PBDTTT-f Series Polymers.** Synthesis of Compound M1. To a solution of 4,6-dibromo-3-fluoro-thieno[3,4-b]thiophene-2-carboxylic acid (0.30 g, 0.83 mmol) in dry toluene (10 mL), oxalyl dichloride (0.21 g, 1.67 mmol) was added slowly. After the addition of two drops of DMF, the reaction mixture was stirred at room temperature for 2 h. Toluene and the remaining oxalyl dichloride were removed under reduced pressure before adding compound A2 (3.87 g, 8.33 mmol) in dry pyridine (10 mL). Then, the reaction mixture was stirred for further 12 h. After the removal of pyridine, the product was extracted with DCM. The organic phase was washed with water and dried over MgSO4. The crude product was purified by column chromatography (SiO2, DCM/PE = 2:1) to afford a pale yellow oil (compound M1) (0.23 g, 34%).

**Synthesis of Compound A1.** To a solution of 3,3,4,5,5,6,7,7,8,8-tridecafluoro-1-octanol (10.00 g, 27.50 mmol), TBAB (0.44 g, 1.38 mmol), and 1,6-dibromohexane (10.10 g, 41.30 mmol) in hexane (60 mL), an aqueous solution of NaOH (20.00 g, 0.50 mol) in water (40 mL) was added slowly. The reactant was heated to 70 °C, stirred for 12 h, and then cooled down to room temperature. After the removal of hexane, the product was extracted with diethyl ether. The organic phase was combined and dried over MgSO4. The organic solvent was evaporated under reduced pressure to yield a yellow oil (compound A1) (8.18 g, 56%). δH (400 MHz; CDCl3/TMS): 3.70 (t, J = 6.9 Hz, 2H), 3.44 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 2.39 (m, 2H), 1.56 (m, 4H), 1.38 (m, 4H). δF (400 MHz; CDCl3): −85.83 (m, 3F), −117.30 (s, 2F). GC−MS m/z: calcd 805.87; found, 805.99. Compounds M2 and M3 were synthesized similarly to compound M1. For compound M2: yield: 0.22 g, 27%. δH (400 MHz; CDCl3/TMS): 4.32 (q, J = 6.5 Hz, 2H), 3.70 (t, J = 6.9 Hz, 2H), 3.44 (t, J = 6.6 Hz, 2H), 2.39 (m, 2H), 1.75 (m, 2H), 1.58 (m, 2H), 1.37 (m, 8H). δF (400 MHz; CDCl3): −81.12 (m, 3F), −113.43 (m, 3F), −118.00 (s, 1F). GC−MS m/z: calcd 733.90; found, 733.86. For compound M3: yield: 0.252 g, 34%. δH (400 MHz; CDCl3/TMS): 4.32 (q, J = 6.5 Hz, 2H), 3.67 (t, J = 6.9 Hz, 2H), 3.43 (t, J = 6.6 Hz, 2H), 2.34 (m, 2H), 1.75 (m, 2H), 1.56 (m, 2H), 1.33 (m, 12H). δF (400 MHz; CDCl3): −85.73 (s, 3F), −117.20 (s, 2F), −118.03 (s, 1F). GC−MS m/z: calcd 661.94; found, 662.07.

**Synthesis of Compound A2.** Compound A1 (5.00 g, 9.48 mmol) was dissolved in a mixture of water (15 mL) and NMP (85 mL). The reaction mixture was heated to 100 °C for 5 days before cooling down to room temperature. After the addition of the saturated aqueous solution of NaCl (200 mL), the aqueous phase was extracted with diethyl ether. The organic phase was washed with water and dried over MgSO4. After the removal of the solvent, the residue was purified by column chromatography (SiO2, DCM) to afford a pale yellow oil (compound A2) (2.22 g, 50%). δH (400 MHz; CDCl3/TMS): 3.69 (t, J = 6.9 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 3.44 (t, J = 6.5 Hz, 2H), 2.39 (m, 2H), 1.56 (m, 4H), 1.38 (m, 4H). δF (400 MHz; CDCl3): −81.12 (m, 3F), −113.58 (m, 2F), −122.04 (m, 2F), −123.02 (m, 2F), −123.82 (m, 2F), −126.30 (m, 2F). GC−MS m/z: calcd 464.10; found, 464.18. Compounds B2 and C2 were synthesized with a protocol similar to that used to synthesize compound A2. For compound B2: yield: 3.88 g, 64%. δH (400 MHz; CDCl3/TMS): 3.69 (t, J = 6.9 Hz, 2H), 3.62 (t, J = 6.6 Hz, 2H), 3.43 (t, J = 6.6 Hz, 2H), 1.55 (m, 4H), 1.32 (s, 8H). δF (400 MHz; CDCl3): −81.18 (m, 3F), −113.78 (m, 2F), −124.72 (m, 2F), −126.14 (m, 2F). GC−MS m/z: calcd 392.14; found, 392.29. For compound C2: yield: 6.46 g, 55%. δH (400 MHz; CDCl3/TMS): 3.66 (t, J = 6.9 Hz, 2H), 3.61 (t, J = 6.6 Hz, 2H), 3.42 (t, J = 6.6 Hz, 2H), 2.33 (m, 2H), 1.55 (m, 4H), 1.28 (s, 12H). δF (400 MHz; CDCl3): −85.83 (3F), −117.30 (s, 2F). GC−MS m/z: calcd 320.18; found, 320.32.

DOI: 10.1021/acsomega.7b00468

ACS Omega 2017, 2, 2489−2498

ACS Omega
under vacuum (0.25 g, 82%). Anal. Calcd for C₅₅H₆₄F₆O₃S₆: C, 53.64; H, 4.84%.  
High-temperature GPC (1,2,4-trichlorobenzene, 160 °C): Mₙ = 22.5 kg·mol⁻¹, Mₘ = 31.8 kg·mol⁻¹, PDI = 1.41. Polymers PBDTTT-F9 and PBDTTT-F5 were synthesized similarly to PBDTTT-F13. For PBDTTT-F9: yield: 0.24 g, 88%. Anal. Calcd for C₅₅H₆₄F₆O₃S₆: C, 53.64; H, 4.84%.

Fabrication of Polymer Solar Cells. The ITO substrates were cleaned by a sequential ultrasonic procedure in an aqueous solution of detergent, distilled water, acetone, and isopropanol. The cleaned ITO substrates were dried at 150 °C to remove the trace amount of solvent.

The configuration of PSCs was ITO/PEDOT:PSS (~40 nm)/polymer:PC₇₁BM/Ca (~20 nm)/Al (~80 nm). The cleaned ITO substrates were treated with UV-ozone. PEDOT:PSS was filtered through a 0.45 μm filter and spin-coated onto the ITO surface. Subsequently, the ITO substrates with PEDOT:PSS films were moved into an oven at 150 °C for 15 min. The blend solution with 10 mg of polymer and 15 mg of PC₇₁BM in 1 mL of o-DCB was spin-coated on the ITO substrates. On top of the active layer to be 0.04 cm².

All of these operations except for the preparation of PEDOT:PSS films were conducted in a nitrogen-filled glovebox.

REFERENCES

(1) Ye, L.; Zhang, S.; Huo, L.; Zhang, M.; Hou, J. Molecular Design toward Highly Efficient Photovoltaic Polymers Based on Two-Dimensional Conjugated Benzothiophene. Acc. Chem. Res. 2014, 47, 1595–1603.

(2) Liu, Y.; Zhao, J.; Li, Z.; Ma, C.; Ma, W.; Hu, H.; Jiang, K.; Lin, H.; Ade, H.; Yan, H. Aggregation and Morphology Control Enables Multiple Cases of High-Efficiency Polymer Solar Cells. Nat. Commun. 2014, 5, 5293.

(3) Zhou, Y.; Fuentes-Hernandez, C.; Shim, J.; Meyer, J.; Giordano, A. J.; Li, H.; Winget, P.; Papadopoulos, T.; Cheun, H.; Kim, J.; Feniol, M.; Dindar, A.; Haske, W.; Najafabadi, E.; Khan, T. M.; Sojoudi, H.; Barlow, S.; Graham, S.; Bredas, J.-L.; Marder, S. R.; Kahn, A.; Kippelen, B. A Universal Method to Produce Low-Work Function Electrodes for Organic Electronics. Science 2012, 336, 327–332.

(4) Genene, Z.; Wang, J.; Meng, X.; Ma, W.; Xu, X.; Yang, R.; Mammo, W.; Wang, E. High Bandgap (1.9 eV) Polymer with over 8% Efficiency in Bulk Heterojunction Solar Cells. Adv. Electron. Mater. 2016, 2, 160088.

(5) Zhao, J.; Li, Y.; Yang, G.; Jiang, K.; Lin, H.; Ade, H.; Ma, W.; Yan, H. Efficient Organic Solar Cells Processed from Hydrocarbon Solvents. Nat. Energy 2016, 1, 15027.

(6) Zhang, Q.; Gan, X.; Liu, F.; Kan, B.; Li, M.; Feng, H.; Zhang, H.; Russell, T. P.; Chen, Y. Evaluation of Small Molecules as Front Cell Donor Materials for High-Efficiency Tandem Solar Cells. Adv. Mater. 2016, 28, 7008–7012.

(7) Huang, Y.; Kramer, E. J.; Heeger, A. J.; Bazan, G. C. Bulk Heterojunction Solar Cells: Morphology and Performance Relationships. Chem. Res. 2014, 114, 7006–7043.

(8) Huang, W.; Chandrasekaran, N.; Prasad, S. K. K.; Gann, E.; Thomsen, L.; Kabra, D.; Hodgkiss, J. M.; Cheng, Y.-B.; McNeill, C. R. Impact of Fullerene Mixing Behavior on the Microstructure, Photophysics, and Device Performance of Polymer/Fullerene Solar Cells. ACS Appl. Mater. Interfaces 2016, 8, 29608–29618.

(9) Chirvase, D.; Parisi, J.; Hummelen, J. C.; Dyakonov, V. Influence of Nanomorphology on the Photovoltaic Action of Polymer–Fullerene Composites. Nanotechnology 2004, 15, 1317.

(10) Miller, N. C.; Cho, E.; Junk, M. J. N.; Gysel, R.; Risio, C.; Kim, D.; Sweetnam, S.; Miller, C. E.; Richter, L. J.; Kline, R. J. Use of X-ray Microanalysis, Molecular Simulations, and Spectroscopy to Determine the Molecular Packing in a Polymer- Fullerene Bimolecular Crystal. Adv. Mater. 2012, 24, 6071–6079.

(11) Padinger, F.; Rüttberger, R. S.; Sariciftci, N. S. Effects of Postproduction Treatment on Plastic Solar Cells. Adv. Funct. Mater. 2003, 13, 85–88.

(12) Brabec, C. J.; Gowerisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. Polymer-Fullerene Bulk-Heterojunction Solar Cells. Adv. Mater. 2010, 22, 3839–3856.

(13) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. High-Efficiency Solution Processable Polymer Photovoltaic Cells by Self-Organization of Polymer Blends. Nat. Mater. 2005, 4, 864–868.

(14) Collins, B. A.; Li, Z.; Tumbleston, J. R.; Gann, E.; McNeill, C. R.; Ade, H. Absolute Measurement of Domain Composition and Nanoscale Size Distribution Explains Performance in PTB7:PC71BM Solar Cells. Adv. Energy Mater. 2013, 3, 65–74.

(15) Moon, J. S.; Takacs, C. J.; Cho, S.; Coffin, R. C.; Kim, H.; Bazan, G. C.; Heeger, A. J. Effect of Processing Additive on the Nanomorphology of a Bulk Heterojunction Material. Nano Lett. 2010, 10, 4005–4008.
Organic Semiconductors Beyond the Molecular Formula. 
Adv. Mater. 2009, 21, 5327–5334.

(18) Slota, J. E.; Ho, X.; Huck, W. T. S. Controlling Nanoscale Morphology in Polymer Photovoltaic Devices. Nano Today 2010, 5, 231–242.

(19) Brabec, C. J.; Heeney, M.; McCulloch, I.; Nelson, J. Influence of Blend Microstructure on Bulk Heterojunction Organic Photovoltaic Performance. Chem. Soc. Rev. 2011, 40, 1185–1199.

(20) Kim, J. S.; Lee, Y.; Lee, J. H.; Park, J. H.; Kim, J. K.; Cho, K. High-Efficiency Organic Solar Cells Based on End-Functional-Group-Modified Poly(3-hexylthiophene). Adv. Mater. 2010, 22, 1355–1360.

(21) Sun, Y.; Chien, S.-C.; Yip, H.-L.; Chen, K.-S.; Zhang, Y.; Davies, J. A.; Chen, F.-C.; Lin, B.; Jen, A. K.-Y. Improved Thin Film Morphology and Bulk-Heterojunction Solar Cell Performance through Systematic Tuning of the Surface Energy of Conjugated Polymers. J. Mater. Chem. 2012, 22, 5587–5595.

(22) Meyer, F. Fluorinated Conjugated Polymers in Organic Bulk Heterojunction Photovoltaic Solar Cells. Prog. Polym. Sci. 2015, 47, 70–91.

(23) Honyak, P. D.; Tinkham, J.; Lahti, P. M.; Coughlin, E. B. Thieno[3,4-b]thiophene Acceptors with Alkyl, Aryl, Perfluoroalkyl, and Perfluorophenyl Pendants for Donor–Acceptor Low Bandgap Polymers. Macromolecules 2013, 46, 8873–8881.

(24) Huo, L.; Li, Z.; Guo, X.; Wu, Y.; Zhang, M.; Ye, L.; Zhang, S.; Hou, J. Benzodifuran-alt-thienothiophene Based Low Band Gap Copolymers: Substituent Effects on Their Molecular Energy Levels and Photovoltaic Properties. Polym. Chem. 2013, 4, 3047–3056.

(25) Sun, H.; Wang, W.; Xu, T.; Liang, Y.; Wu, Y.; Li, G.; Yu, L. Synthesis of Fluorinated Polythienothiophene-co-benzothiadiazines and Effect of Fluorination on the Photovoltaic Properties. J. Am. Chem. Soc. 2011, 133, 1885–1894.

(26) Li, G.; Gong, X.; Zhang, J.; Liu, Y.; Feng, S.; Li, C.; Bo, Z.; 4-Alkyl-3,5-difluorophenyl-Substituted Benzodithiophene-Based Wide Band Gap Polymers for High-Efficiency Polymer Solar Cells. ACS Appl. Mater. Interfaces 2016, 8, 3686–3692.

(27) Oh, J.; Krantihiara, K.; Lee, C.; Gunasekar, K.; Kim, S.; Ma, B.; Kim, B. J.; Jin, S.-H. Side-Chain Fluorination: An Effective Approach to Achieving High-Performance All-Polymer Solar Cells with Efficiency Exceeding 7%. Adv. Mater. 2016, 28, 10016–10023.

(28) Zhou, H.; Yang, L.; Stuart, A. C.; Price, S. C.; Liu, S.; You, W. Development of Fluorinated Benzothiadiazole as a Structural Unit for a Polymer Solar Cell of 7% Efficiency. Angew. Chem., Int. Ed. 2011, 50, 2995–2998.

(29) Price, S. C.; Stuart, A. C.; Yang, L.; Zhou, H.; You, W. Fluorine Substituted Conjugated Polymer of Medium Band Gap Yields 7% Efficiency in Polymer–Fullerene Solar Cells. J. Am. Chem. Soc. 2011, 133, 4625–4631.

(30) Zhang, A.; Wang, Q.; Bowee, R. A. A.; Li, C.; Zhang, J.; Zhou, Y.; Wei, Z.; Li, Y.; Janssen, R. A. J.; Wang, Z.; Li, W. Perfluoroalkyl-Substituted Conjugated Polymers as Electron Acceptors for All-Polymer Solar Cells: The Effect of Diodoperfluoroalkane Additives. J. Mater. Chem. A 2016, 4, 7736–7745.

(31) Wang, C.; Mueller, C. J.; Gann, E.; Liu, A. C. Y.; Thelakkat, M.; McNeill, C. R. Influence of Fluorination on the Microstructure and Performance of Diketopyrrolopyrrole-Based Polymer Solar Cells. J. Polym. Sci., Part B: Polym. Phys. 2017, 55, 49–59.

(32) Liao, S.-H.; Jhuo, H.-J.; Cheng, Y.-S.; Chen, S.-A. Fullerene Derivative-Doped Zinc Oxide Nanofilm as the Cathode of Inverted Polymer Solar Cells with Low-Bandgap Polymer (PTB7-Th) for High Performance. Adv. Mater. 2013, 25, 4766–4771.

(33) Bencheikh, F.; Duchê, D.; Ruiz, C. M.; Simon, J.-J.; Escoubas, L. Study of Optical Properties and Molecular Aggregation of Conjugated Low Band Gap Copolymers: PTB7 and PTB7-Th. J. Phys. Chem. C 2015, 119, 24643–24648.