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Side chain effect on difluoro-substituted dibenzo[a,c]phenazine based conjugated polymers as donor materials for high efficiency polymer solar cells

Guangwu Li, Zhen Lu, Cuihong Li, Zhishan Bo

Two conjugated polymers with benzodithiophene derivatives as the donor unit and planar difluoro-substituted dibenzo[a,c]phenazine as the acceptor unit P1, P2-L and P2-H were designed, synthesized, and used as the donor material used in the polymer solar cells. P2-H exhibit the highest hole mobility with $1.54 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$. Polymer solar cells (PSCs) with the blend of P1:PC71BM (1:1.5, by weight) as the active layer show the highest power conversion efficiency (PCE) of 6.0% in those polymers with an open circuit voltage ($V_{oc}$) of 0.74 V, a short circuit current (J$_{sc}$) of 12.50 mA/cm$^2$, and a fill factor (FF) of 0.65.

RESULTS AND DISCUSSION

Material Synthesis and Characterization

The syntheses of monomers and polymers are outlined in Scheme 1. Compound 1 was synthesized according to the literature procedures. The solubility and electronic properties of quinoxaline derivatives can be tuned by the variation of the substituents. D-A polymers with planar quinoxaline acceptor unit exhibit much better photovoltaic performance than the corresponding less planar quinoxaline acceptor unit. Dibenzo[a,c]phenazine has been used to construct many D-A alternating conjugated polymers. In addition, the introduction of fluoro substituents on the acceptor units has been demonstrated to be a very efficient strategy to improve PCE of PSCs, fluorine substituents can lower the HOMO and LUMO energy levels of resulted conjugated polymers to afford higher open circuit voltage ($V_{oc}$), increase the intramolecular polymer chain interaction to have higher hole mobility, and reduce the charge recombination to achieve higher efficiency.
compound 2 with Br₂ in CH₂Cl₂ afforded M1 in a yield of 91%. The polymerization of M1 with M2 and M3 afforded P1 and P2, respectively. P2 was fractioned into low molecular weight fraction (P2-L) and high molecular weight fraction (P2-H) according to their solubility in chloroform. P2-L can be dissolved in hot chloroform. P1 and P2-H exhibited limited solubility in common chlorinated organic solvents such as CB, DCB, and TCB at room temperature, but can be fully dissolved in these solvents at elevated temperature. Molecular weights and their distributions were measured by gel permeation chromatography (GPC) using TCB as an eluent at 150 °C. Molecular weights measurements from 20 to 300 °C under nitrogen atmosphere shown in Table 1. Differential scanning calorimetry (DSC) showed that there is no obvious glass transition for these polymers are of good thermal stability as indicated by thermo gravimetric analysis (TGA) measurements. The 5% decomposition temperatures of P1, P2-L, and P2-H are also shown in Table 1. Differential scanning calorimetry (DSC) measurements from 20 to 300 °C under nitrogen atmosphere showed that there is no obvious glass transition for these polymers. Powdery X-ray diffraction (XRD) measurements were carried out to investigate the packing of polymer chains in solid state. As shown in Figure 1, XRD diffraction patterns of P1 exhibited two diffraction peaks. The first peak at small angle region, which reflects the distance of polymer backbones separated by the flexible side chains, is located at 2θ of 5.14 °, corresponding to a distance of 17.2 Å. The second peak at the wide angle region reflex the π-π stacking distances between polymer backbones, which is located at 2θ of 22.6 °, corresponding to a distance of 3.9 Å. P2-L and P2-H exhibit only a broad peak in the wide angle region, which is located at 20.9 °, corresponding to a distance of 4.3 Å. For P2, the lack of diffraction peak in small angle region indicated that P2 formed a less ordered packing in solid state as compared with P1. Compared with P1, the larger π-π stacking distance of P2 in the solid state refexxes that the two 4,5-didecylthienyl substituents at the 4,8-position of benzodithiophene can prevent the close and ordered packing of polymer chains in the solid state. The results are consistent with the photovoltaic device results.

Scheme 1. Synthetic route of P1 and P2

\[ \text{M1} \rightarrow \text{P1} \]

\[ \text{M2} \rightarrow \text{P2} \]

\[ \text{M3} \rightarrow \text{P2} \]

i) Zn, AcOH; ii) phenanthrene-9,10-dione, 80 °C; iii) NBS, CHCl₃, rt; vi) toluene/DMF (v:v, 10:1), Pd(PPh₃)₄, reflux.

Table 1. Physical Properties of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_n ) (kg/mol) (^a)</th>
<th>( M_w ) (kg/mol) (^a)</th>
<th>D</th>
<th>( T_d ) (°C) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>28.0</td>
<td>59.9</td>
<td>2.38</td>
<td>318</td>
</tr>
<tr>
<td>P2-L</td>
<td>34.7</td>
<td>72.6</td>
<td>2.09</td>
<td>427</td>
</tr>
<tr>
<td>P2-H</td>
<td>63.7</td>
<td>113.2</td>
<td>1.77</td>
<td>439</td>
</tr>
</tbody>
</table>

\(^a\) \( M_n \), \( M_w \), and dispersity (D) of polymers were determined by GPC at 150 °C using polystyrene standards with TCB as an eluent. \(^b\) Decomposition temperatures were determined by TGA under N₂ based on 5% weight loss.
Optical Properties. Optical properties of P1 and P2 in solutions and as thin films are investigated by UV-visible absorption spectroscopy and shown in Figure 2. The optical properties of low and high molecular weight polymer P2 are exactly the same, so here we did not differentiate P2-L and P2-H. UV-vis absorption spectra of P1 and P2 in dilute DCB solutions and as thin films are shown in Figure 2. In solutions both P1 and P2 exhibit a broad absorption with two peaks in the visible region. The absorption peaks are located at 431 and 614 nm for P1 and 421 and 591 nm for P2. Compared with their solution absorption spectra, the corresponding film ones were red-shifted due to the aggregation of polymer chains in the solid state. All the solution and film optical absorption data are summarized in Table 2. The film absorption onsets (\(\lambda_{\text{edge}}\)) of P1 and P2 are 747 and 729 nm, respectively. The optical band gaps (\(E_{\text{g,opt}}\)) of P1 and P2 were therefore calculated to be 1.66 and 1.70 eV, respectively, according to the equation: 

\[
E_{\text{g,opt}} = \frac{1240}{\lambda_{\text{edge}}} \text{eV}
\]

Electrochemical Properties. Electrochemical properties of P1, P2-L, and P2-H were investigated by cyclic voltammetry (CV) using a standard three electrodes electrochemical cell. As shown in Figure 3, these three polymers exhibited irreversible redox processes. The onset oxidation potentials of P1, P2-L, and P2-H are 0.59, 0.80, and 0.80 V, respectively. HOMO levels of P1, P2-L, and P2-H were determined, using the equation 

\[
E_{\text{HOMO}} = \frac{-e(E_{\text{ox}} + 4.71)}{2}
\]

To be -5.30, -5.51, and -5.51 eV, respectively. LUMO levels of P1, P2-L, and P2-H were therefore calculated according to the equation 

\[
E_{\text{LUMO}} = E_{\text{HOMO}} + \frac{1240}{\lambda_{\text{edge}}}
\]

The data are also summarized in Table 2.

Transport Properties. Hole mobility up to \(10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) is usually required for polymer donors in order to obtain balanced electron and hole mobility for the polymer and PCBM blends, and balanced mobility is very crucial for achieving high performance polymer solar cells. Transport properties of polymers were therefore investigated by fabrication of field effect transistors (FETs). Bottom-contact devices were fabricated on Si/SiO\(_2\) substrates with the low resistance Si as channel width, \(L\) is the channel length, \(C_i\) is the capacitance per unit area of the gate dielectric layer (SiO\(_2\), 500 nm, \(C_i = 11\ \text{nF/cm}^2\)), and \(V_G\) and \(V_T\) is the gain voltage and threshold voltage, respectively. Hole mobilities, \(V_T\), and on/off ratios are summarized in Table 3, the detailed data are shown in Table S1. Transfer characteristic and output characteristic of polymers are shown in Figure S1. Hole mobilities of these polymers are close to the electron mobility of PC\(_{71}\)BM.

**Table 2.** Electrochemical and optical properties of polymers.

<table>
<thead>
<tr>
<th>polymer</th>
<th>(\lambda_{\text{max}}) [nm]</th>
<th>(\lambda_{\text{max}}) [nm]</th>
<th>(\lambda_{\text{edge}}) [nm]</th>
<th>(E_{\text{g,opt}}) [eV]</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>431, 614</td>
<td>442, 631</td>
<td>746</td>
<td>1.66</td>
<td>-5.30</td>
<td>-3.64</td>
</tr>
<tr>
<td>P2-L</td>
<td>421, 591</td>
<td>453, 631</td>
<td>729</td>
<td>1.70</td>
<td>-5.51</td>
<td>-3.81</td>
</tr>
</tbody>
</table>

* measured at 100 °C. \(^b\) calculated from the absorption band edge of the copolymer film, \(E_{\text{g,opt}} = \frac{1240}{\lambda_{\text{edge}}}\) calculated by the equation 

\[
E_{\text{HOMO}} + \frac{1240}{\lambda_{\text{edge}}}
\]

\(^c\) calculated by the equation 

\[
E_{\text{LUMO}} = E_{\text{HOMO}} + \frac{1240}{\lambda_{\text{edge}}}
\]

**Table 3.** FET properties of the pure polymer films.

<table>
<thead>
<tr>
<th>polymers</th>
<th>Annealing temperature</th>
<th>on/off</th>
<th>(\mu) (cm(^2)/Vs)</th>
<th>(V_T) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>200 °C</td>
<td>1.07±0.17×10(^7)</td>
<td>3.56±0.87×10(^3)</td>
<td>-1.5±0.7</td>
</tr>
<tr>
<td>P2-L</td>
<td>200 °C</td>
<td>1.47±0.20×10(^6)</td>
<td>4.31±0.12×10(^3)</td>
<td>-22.8±0.9</td>
</tr>
<tr>
<td>P2-H</td>
<td>250 °C</td>
<td>9.29±0.71×10(^6)</td>
<td>1.45±0.09×10(^2)</td>
<td>-8.4±0.9</td>
</tr>
</tbody>
</table>
Photovoltaic Properties. Photovoltaic properties of polymers were evaluated by using the device configuration of ITO/ZnO/active layer/MoO3/Ag. The performance of devices was optimized by variation of the weight ratio of polymer to PC71BM, the concentration of blend solution, and the spin-coating speed. J-V curves of PSCs based on these three polymers are illustrated in Figure 4(a). For P1, devices fabricated with the blends of P1 and PC71BM in a weight ratio of 1:1.5 in DCB solutions gave the best device performance with a PCE of 6.0%, a $V_{oc}$ of 0.74 V, a $J_{sc}$ of 12.50 mA/cm², and an FF of 0.65. Devices fabricated with the blends of P2-L and PC71BM in a weight ratio of 1:1.5 in DCB solutions gave the best device performance with a PCE of 1.7%, a $V_{oc}$ of 0.93 V, a $J_{sc}$ of 4.54 mA/cm², and an FF of 0.40. For P2-H, a PCE of 2.8% with a $V_{oc}$ of 0.94 V, a $J_{sc}$ of 5.90 mA/cm², and an FF of 0.50 can be achieved with device fabricated under the same conditions like P2-L, and the data are summarized in Table 4. Ten devices were fabricated to give the average value of PCEs, the detailed results are shown in Table S2. The use of 1,8-diiodooctance (DIO) as the solvent additive for the processing of the active layer has been tried, but the photovoltaic performances are inferior to DIO free ones.

As shown in Figure 4(b), external quantum efficiencies (EQEs) were measured to examine the accuracy of $J_{sc}$, the devices was fabricated from the best conditions for each polymers. For P1, EQE value approached 0.6, leading to a high short circuit current for the devices. In comparison with P1 based devices, P2 based PSCs exhibited lower EQEs. The EQE value of P2-H based devices is higher than that of P2-L based devices. As observed for many conjugated polymers, high molecular weight materials usually gave high hole mobility and efficiency.

Film Morphology. Usually, the extension of lateral conjugation of conjugated polymers can give higher photovoltaic performance;¹⁹ therefore, P2 with two thienyl substituents on the benzodithiophene unit was anticipated to afford high PCE. To understand why P1:PC71BM based PSCs
gave much higher PCE than P2-PC71BM based PSCs. Nanostructures of blend films were therefore investigated by transmission electron microscopy (TEM), and the TEM images are shown in Figure 5. TEM investigations revealed that P1:PC71BM blend films are homogenous with nanoscale phase separation; whereas P2-L:PC71BM and P2-H:PC71BM blend films are of apparent phase separation with the domain size approximate to 100 nm. The large domains are probably formed by the aggregation of PC71BM, indicating the poor miscibility between P2 and PC71BM. The formation of large isolated spherical aggregation of PC71BM is detrimental to the transportation of electron to the collecting electrode.

Conclusions
We have designed and synthesized two conjugated polymers based on difluoro-substituted dibenzo[a,c]phenazine and benzodithiophene derivations. The as-synthesized two polymers were carefully characterized and used as the donor material in the BHJ PSCs. P1 gave the best device performance with PCE of 6.0%, a \(V_{oc}\) of 0.74 V, and a \(J_{sc}\) of 12.50 mA/cm\(^2\). Both the main chain and side chain play important roles to the performance of polymer solar cells. The optical property is mainly determined by the main chain structures; whereas the side chains can significantly influence the morphology of blend films. If the polymers have similar optical properties, their photovoltaic performance can be enhanced by optimizing the morphology of blend films through changing different side chains. Influences of side chains and the molecular weight on the photovoltaic performance of PSCs were also investigated. Compared to P1, P2-H with two lateral 2,3-didecylthiophene on the benzodithiophene unit has high molecular weight and better solubility in commonly used organic solvents. The formation of large aggregations in the P2-H:PC71BM blend films made the photovoltaic performance of P2-H inferior to that of P1.

Acknowledgements
We express thanks for the financial support by the NSF of China (51003006 and 2116160443), the 973 Programs (2011CB935702), and the Fundamental Research Funds for the Central Universities.

Notes and references


