Development of New Conjugated Polymers with Donor−π-Bridge−Acceptor Side Chains for High Performance Solar Cells

Fei Huang,[†,‡] Kung-Shih Chen,[†] Hin-Lap Yip,[†] Steven K. Hau,[†] Orb Acton,[†] Yong Zhang,[†] Jingdong Luo,[†] and Alex K.-Y. Jen*,[†]

Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195-2120, and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China

Received February 9, 2009; E-mail: ajen@u.washington.edu

Polymeric solar cells (PSCs) have attracted considerable attention in recent years due to their potential for low cost, lightweight, and good compatibility with the roll-to-roll process for making flexible large area devices.[1] Bulk-heterojunction-type solar cells use a phase-separated blend of organic electron donor and acceptor components, where the conjugated polymer is often used as the donor and the fullerene derivative is used as the acceptor. Among several widely investigated topics in this area is the development of small band gap (<2.0 eV) conjugated polymers as an efficient electron donor for solar cells.[2] Currently, one of the most promising donors is poly(3-hexylthiophene) (P3HT), and the power conversion efficiency (PCE) of PSCs based on its thin film blend with [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM) has often reached ∼4−5%.[3] However, it is difficult to further improve the efficiency of P3HT-based PSCs due to its absorption not matching well with the solar spectrum and the relatively small energy level offset between its highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PC$_{61}$BM which limits the magnitude of the short circuit current and open circuit voltage.[4] To optimize the material properties, conjugated polymers with alternating electron-rich and -deficient units along their backbone have been extensively developed due to their absorption spectra and band gap can be readily tuned by controlling the intramolecular charge transfer (ICT) from the donors to the acceptors. Using this approach, several narrow band gap donor−acceptor type (D−A) conjugated polymers have shown promising performances with the PCE as high as ∼3−6%.[5] However, in these linear D−A polymers, the molecular interactions and packing orientation of the conjugating moieties need to be carefully controlled to ensure proper processability and charge transporting properties.[2,6]

To provide a simple and generally applicable method for improving the properties of active materials, we have designed and synthesized a series of new conjugated polymers with D−π-bridge−A side chains for high efficiency PSCs. Here, we report two representative polymers, PFDCN and PFPDT (Figure 1). Different from the common linear D−A conjugated polymers,[2] the acceptors of PFDCN and PFPDT are located at the ends of the side chains and connected with the triphenylamine donors on the main chain through a styrylthiophene π-bridge. Hence, the designed polymers have an electron-rich conjugated main chain with a D−π-bridge−A conjugated side chain. This new design takes advantage of the well-established knowledge of nonlinear optical chromophores to optimize the absorption spectra and energy levels of the resultant polymers.[7] Previously, it has been reported that the fluorene−triarylamine copolymer which

† University of Washington.
‡ South China University of Technology.

has a structure analogous to that of the electron-rich main chain of PFDCN and PFPDT exhibited a high hole mobility of 0.01 cm^2 V^{-1} s^{-1}.[8] In addition to these features, the two-dimensional conjugated structure of these polymers may improve their isotropic charge transport, which is important for PSCs.[6] Based on this design concept, the PSCs using the blend of PFDCN and PFPDT with fullerene derivatives exhibit promising performance with a PCE up to 4.74% and 4.37%, respectively.
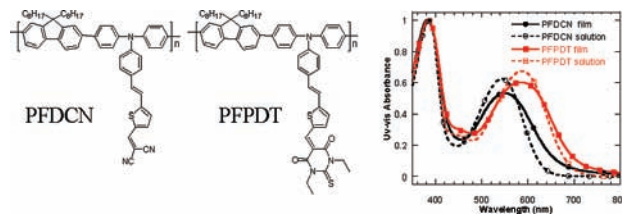

Figure 1. Structures of polymers and absorption spectra of polymers solution in chloroform and as a film.

PFDCN and PFPDT were obtained by a Knoevenagel condensation between an aldehyde-containing conjugated precursor polymer and malononitrile and diethylthiobarbituric acid, respectively (see Supporting Information (SI)). Due to their side chains, both polymers are amorphous and have good solubility in common organic solvents such as chloroform and chlorobenzene. The weight-average molecular weights of PFDCN and PFPDT are 17.7 and 16.3 kg/mol with a polydispersity index of 1.7 and 1.6, respectively. Differential scanning calorimetry (DSC) studies shows that the glass transition temperatures (T_g) are 155 and 163 °C for PFDCN and PFPDT, respectively. No crystallization or melting peak is observed upon further heating beyond the T_g. Absorption spectra of the polymers in solution are shown in Figure 1. Both of them show two obvious absorption peaks, where the first absorption peaks at ∼385 nm are corresponding to the π−π* transition of their conjugated main chains and the others are corresponding to the strong ICT characters of their side chains. The optical band gap of PFDCN calculated from the onset of the film absorption is 1.87 eV. By using a stronger acceptor, PFPDT exhibits an obvious red-shifted ICT peak compared to PFDCN, corresponding to a smaller optical band gap of 1.76 eV. The energy level of the polymer was investigated by cyclic voltammetry (CV). The HOMO energy levels of PFDCN and PFPDT are calculated to be −5.30 and −5.26 eV by using the ferrocene value of −4.8 eV below the vacuum as the internal standard. The LUMO levels of PFDCN and PFPDT are −3.43 and −3.50 eV by estimating from their optical band gaps and HOMO energy levels. Clearly, both of the polymers exhibit similar HOMO energy levels due to their same donor main chain,

while their LUMO energy levels are dictated by the acceptors on the side chains.

The photovoltaic properties of PFDCN and PFPDT were studied in PSCs using $PC_{61}BM$ or [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as the acceptor in a conventional device configuration of ITO/PEDOT:PSS(40 nm)/polymer:PCBM(1:4, w/w 85 nm)/Ca(10 nm)/Al(100 nm) (ITO: indium tin oxide; PEDOT:PSS: poly(styrene sulfonate)- doped poly(ethylene-dioxythiophene); PCBM: $PC_{61}BM$ or $PC_{71}BM$. A detailed device fabrication process is described in the SI. The area of the device was determined by the size of the cathode, which was 3.14×10^{-2} cm^2. The $PC_{71}BM$ was chosen as the acceptor because it has electronic properties similar to those of $PC_{61}BM$ but a much stronger absorption in the visible region with a broad peak from 440 to 530 nm,[9] which can complement the absorption valley of the polymers (Figure 1).
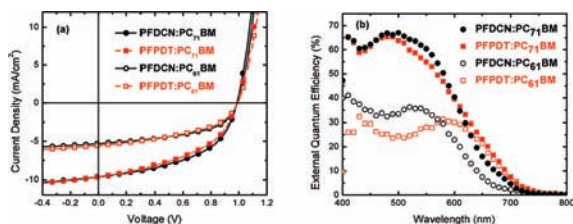

Figure 2. (a) $J-V$ curves of PFDCN and PFPDT-based solar cells under AM 1.5G illumination. (b) External quantum efficiency spectrum of PFDCN and PFPDT-based solar cells.

Both of the polymers exhibit promising photovoltaic properties with an average PCE (from eight devices for each polymer) of 4.47% and 4.19% for PFDCN and PFPDT, respectively, in $PC_{71}BM$-based devices. Figure 2a shows the current density–voltage ($J-V$) curves of the best devices under the illumination of simulated AM 1.5G conditions (100 mW/cm^2). The detailed procedures for characterization are listed in the SI. PCEs up to 4.74% were observed for the PFDCN:$PC_{71}BM$ solar cells with an open circuit voltage (V_{OC}) of 0.99 V, a short circuit current density (J_{SC}) of 9.62 mA/cm^2, and a fill factor of 50.0%. The maximum PCE of PFPDT:$PC_{71}BM$ solar cells also reaches 4.37% with a V_{OC} of 0.99 V, a J_{SC} of 9.61 mA/cm^2, and a fill factor of 46.0%. For comparison, the $J-V$ curves and the external quantum efficiencies (EQEs) of $PC_{61}BM$ devices are also shown in Figure 2. A significant drop in J_{SC} was observed in both $PC_{61}BM$ devices, indicating the importance of the complementary absorption of $PC_{71}BM$. Figure 2b shows the EQE of the devices illuminated by monochromatic light. The results from the EQE study clearly showed the photocurrent increments of $PC_{71}BM$ devices because of the enhanced absorption from $PC_{71}BM$.

It is interesting that the PSC device performance based on PFDCN and PFPDT is comparable to those of the state-of-the-art works based on linear narrow band gap D–A conjugated polymers.[2,5] Several factors contribute to their excellent photovoltaic properties. First, both PFDCN- and PFPDT-based PSC devices exhibited a much higher V_{oc} (0.99 V) compared to most of the devices based on the previously reported small band gap materials,[2] due to their relatively low HOMO level, which can be readily controlled by adjusting the main chain donor. Second, their absorption spectra can be easily tuned by controlling the acceptor strength of their side chains or by using a more efficient π-bridge, without disturbing their conjugated main chain structures. Originally, there are some concerns that PFDCN and PFPDT may possess low hole mobility because of their amorphous nature and bulky and rigid side chains.

Hence, a detailed hole mobility study of the polymers:$PC_{71}BM$ blend films was conducted by using the space-charge-limited-current (SCLC) method. The SCLC measurements have been widely used to estimate the charge transporting ability of the PSC active layers.[10] The blend films exhibited a hole mobility of 5.27×10^{-4} cm^2 V^{-1} s^{-1} for PFDCN and 1.16×10^{-3} cm^2 V^{-1} s^{-1} for PFPDT, respectively, which is even higher than that of P3HT in a similar device configuration.[10] Considering their two-dimensional conjugated structure, PFDCN and PFPDT may have better isotropic charge transport ability than linear polymers, which is beneficial for PSC applications.

In conclusion, two new conjugated polymers PFDCN and PFPDT have been designed and synthesized. Both of them exhibit excellent photovoltaic properties with a PCE as high as 4.74%. This approach provides great flexibility in fine-tuning the absorption spectra and energy levels of the resultant polymers for achieving high device performance.

Supporting Information Available: Experimental details of the synthesis of the polymer, the fabrication and characterization of the devices, measurements and instruments. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Gnes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324.
(2) Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; De Boer, B. *Polym. Rev.* **2008**, *48*, 531.
(3) (a) Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864. (b) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K. H.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617. (c) Yip, H.-L.; Hau, S. K.; Baek, N. S.; Ma, H.; Jen, A. K.-Y. *Adv. Mater.* **2008**, *20*, 2376. (d) Hau, S. K.; Yip, H.-L.; Ma, H.; Jen, A. K.-Y. *Appl. Phys. Lett.* **2008**, *93*, 233304.
(4) Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. *Adv. Mater.* **2006**, *18*, 789.
(5) (a) Mühlbacher, D.; Scharber, M.; Morana, M.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C. *Adv. Mater.* **2006**, *18*, 2884. (b) Wang, E.; Wang, L.; Lan, L.; Luo, C.; Zhuang, W.; Peng, J.; Cao, Y. *Appl. Phys. Lett.* **2008**, *92*, 033307. (c) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletete, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2008**, *130*, 732. (d) Baek, N. S.; Hau, S. K.; Yip, H.-L.; Acton, O.; Chen, K.-S.; Jen, A. K.-Y. *Chem. Mater.* **2008**, *20*, 5734. (e) Hou, J. H.; Chen, H.-Y.; Zhang, S. Q.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144. (f) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297. (g) Liang, Y. Y.; Feng, D. Q.; Wu, Y.; Tsai, S. T.; Li, G.; Ray, C.; Yu, L. P. *J. Am. Chem. Soc.* **2009**, *131*, 7792.
(6) Roncali, J.; Leriche, P.; Cravino, A. *Adv. Mater.* **2007**, *19*, 2045.
(7) (a) Marder, S. R.; Cheng, L.-T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. *Science* **1994**, *263*, 511. (b) Liu, S.; Haller, M. A.; Ma, H.; Dalton, L. R.; Jang, S.-H.; Jen, A. K.-Y. *Adv. Mater.* **2003**, *15*, 603.
(8) Fong, H. H.; Papadimitratos, A.; Malliaras, G. G. *Appl. Phys. Lett.* **2006**, *89*, 172116.
(9) Yao, Y.; Shi, C. J.; Li, G.; Shrotriya, V.; Pei, Q. B.; Yang, Y. *Appl. Phys. Lett.* **2006**, *89*, 153507.
(10) Mihailetchi, V. D.; Xie, H.; de Boer, B.; Koster, J. A.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 699.

JA9066139