8058 *Macromolecules* **2010**, *43*, 8058–8062
DOI: 10.1021/ma101693d

Macromolecules
ARTICLE

Benzodifuran-Based π-Conjugated Copolymers for Bulk Heterojunction Solar Cells

Hui Li,[†] Peng Jiang,[‡] Chenyi Yi,[†] Chen Li,[†] Shi-Xia Liu,*[,†] Songting Tan,*[,‡] Bin Zhao,[‡] Jörg Braun,[§] Wolfgang Meier,[§] Thomas Wandlowski,[†] and Silvio Decurtins[†]

[†]*Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland,* [‡]*College of Chemistry and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, P. R. China, and* [§]*Departement für Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*

Received July 27, 2010; Revised Manuscript Received September 6, 2010

ABSTRACT: Novel π-conjugated copolymers based on a soluble electroactive benzo[1,2-*b*:4,5-*b*′]difuran (BDF) chromophore have been synthesized by the introduction of thiophene/benzo[*c*][1,2,5]thiadiazole/9-phenylcarbazole comonomer units. These copolymers cover broad absorption ranges from 250 to 700 nm with narrow optical band gaps of 1.71−2.01 eV. Moreover, their band gaps as well as their molecular electronic energy levels are readily tuned by copolymerizing the BDF core with different π-conjugated electron-donating or withdrawing units in different ratios. Bulk heterojunction solar cell devices are fabricated using the copolymers as the electron donor and PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) as the electron acceptor. Preliminary research has revealed power conversion efficiencies of 0.17−0.59% under AM 1.5 illumination (100 mW/cm^2).

Introduction

Bulk heterojunction (BHJ) polymer photovoltaics have attracted particular attention due to the fact that there is the potential to produce low-cost, easily processable, light, and flexible all-organic photovoltaic devices.[1] By blending appropriate electron donor (D) and electron acceptor (A) materials, an interpenetrating network with the optimal morphology favorable for transporting free charge carriers can be achieved. As a consequence, extensive research efforts have been devoted to a rational design and synthesis of electron donor π-conjugated polymers with a low optical band gap, good film-forming properties, miscibility with a given n-type material, and high hole mobility.[2] Specifically, in the case of BHJ devices using [6,6]-phenyl-C_{61}-butyric acid methyl ester as the acceptor, it is desirable to develop conjugated polymers with a band gap between 1.2 and 1.9 eV, simultaneously exhibiting an intense and broad-range absorption spectrum to maximize the light-harvesting ability.[3] Although a variety of π-conjugated polymers, such as polythiophene, polyfluorene, and poly(*p*-phenylenevinylene)s, have been used as the donor components for the BHJ application, the power conversion efficiency (PCE) of the devices is moderate.[4] Recently, the benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) unit has emerged as an attractive donor component for solar cells due to its large planar and conjugated structure, which can promote cofacial $\pi-\pi$ stacking, thus benefiting charge transport.[5] Some BDT-based conjugated polymers for the construction of highly efficient BHJ solar cells have been reported,[3,5−7] leading to a highest PCE of 7.73%.[5b] In contrast, the analogous benzo[1,2-*b*:4,5-*b*′]-difuran (BDF) derivatives proved also to be excellent compounds for high-performance hole-transporting materials,[8] which for instance find applications in multilayer organic light-emitting diodes (OLEDs) and organic field effect transistors (OFETs), but no BDF-based polymers in BHJ application have been reported, perhaps because of very limited synthetic availability.

Recently, we have reported a facile and efficient synthetic route to a fully functionalized BDF derivatives **1** (Figure 1), which for example can readily undergo Suzuki, Heck, and Sonogashira coupling reactions to afford a manifold of extended π-conjugated BDF derivatives.[9] As a continuation of our project, three new π-conjugated copolymers (PBT, PBB, PBP), consisting of planar BDF units incorporated with thiophene/benzothiadiazole/9-phenylcarbazole-based monomers, were synthesized via Sonogashira coupling reactions of the key precursor **1a**. Their electrochemical, photophysical, and photovoltaic performances have been investigated.

Experimental Section

Materials. All the chemicals and solvents were purchased from commercial sources and used without further purification. The monomer **1a**, 2,6-bis(dihexylamino)-4,8-diethynylbenzo-[1,2-*b*:4,5-*b*′]difuran-3,7-dicarbonitrile, was synthesized according to the literature.[9]

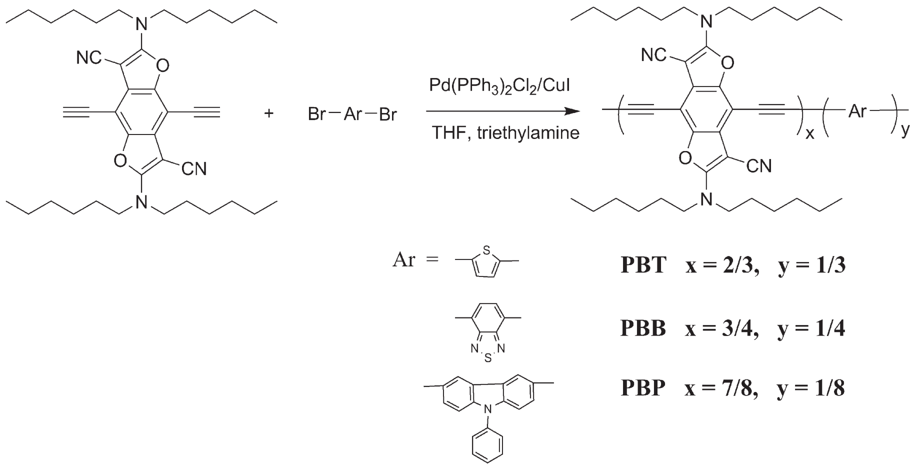
Characterization. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 300 spectrometer operating at 300.18 and 75.5 MHz, respectively. The average molecular weight and polydispersity index (PDI) of the copolymers were determined using Waters1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Thermogravimetric analyses (TGA) were performed under nitrogen on a Mettler Toledo TGA/SDTA 851^e instrument at a heating rate of 5 °C/min. Differential scanning calorimetric measurements (DSC) of the copolymers were conducted under nitrogen on a Mettler Toledo DSC823^e instrument at a heating rate of 5 °C/min. UV−vis absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer. Photoluminescent spectra were recorded on a Perkin-Elmer luminescence spectrometer LS50B. Powder X-ray diffraction measurements were performed on Stoe spellmann generator type DF4 with a Cu anode as the X-ray source (wavelength = 1.54 Å).

Cyclic Voltammetry Measurements. Chloroform (HPLC grade, Acros), acetonitrile (HPLC grade, Aldrich), and tetra-*n*-butylammonium hexafluorophosphate (TBAPF$_6$, electrochemical grade, Fluka) were used as received. Electrochemical

---

*Corresponding authors: Tel +41 31 6314296; fax +41 31 6314399; e-mail liu@iac.unibe.ch (S.-X.L.), tanst2008@163.com (S.T.).

Scheme 1. Synthesis of Copolymers PBT, PBB, and PBP



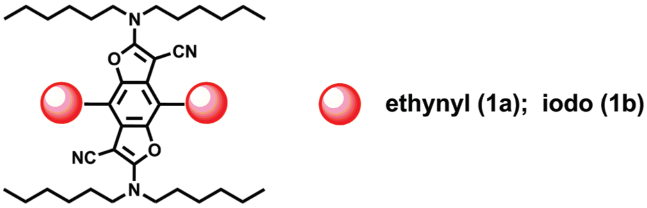


Figure 1. Chemical structures of the fully functionalized benzo[1,2-*b*:4,5-*b*′]difuran (BDF) derivatives.

measurements were carried out in a custom-made single compartment three-electrode cell with a working volume of less than 2 cm^3, containing a Pt coil counter electrode. The reference electrode was a lab-built nonaqueous Ag|AgO_x electrode, contacted to the cell through a low-leakage high-conductance Vycor diaphragm, and was calibrated versus ferrocene in a separate cell after each measurement series. 0.1 M $TBAPF_6$ in acetonitrile was used as the electrolyte. All potentials in this paper are referred to the ferrocene equilibrium potential. The working electrode (WE) was a polycrystalline Pt bead, polished to mirror finish, exposing a geometric surface area of 0.0353 cm^2 in hanging meniscus configuration. The WE was hydrogen flame-annealed before each measurement and cooled in a stream of high-purity Ar. For thin layer cyclic voltammetry, a drop of redox-active compound solution (0.1 mM in $CHCl_3$) was cast on the WE surface and dried. Then, the WE coated by the copolymer was inserted into the cell which contains a solution of 0.1 M $TBAPF_6$ in acetonitrile. The potentiostat was an Autolab PGSTAT30 system (Eco Chemie BV, The Netherlands), and cyclic voltammetry was carried out using the linear scan mode. In all cases, the WE was brought into contact with the electrolyte under potential control, at a potential value in the stablility range of the studied copolymer.

Fabrication and Characterization of Photovoltaic Cells. The photovoltaic cells were constructed in the traditional sandwich structure through several steps. The ITO-coated glass substrates were first cleaned by ultrasonic treatment in ethanol and isopropyl alcohol, successively, and then treated by Ar/O_2 plasma for 5 min. Poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT:PSS, from Bayer AG) was spin-coated from an aqueous solution on a cleaned ITO/glass substrate giving a thickness of about 30 nm, and it was dried subsequently at 150 °C for 30 min. The photoactive blend layer of copolymer and PCBM was prepared by spin-coating a chlorobenzene solution (24 mg/mL) of the copolymers and PCBM (1:4, w/w) on top of the PEDOT:PSS layer at a spin speed of 4000 rpm for 30 s and then annealed at 150 °C for 5 min in a nitrogen-filled glovebox. Finally, the substrates were transferred into an evaporator and pumped down to 4×10^{-4} Pa. Subsequently, the cathode of devices, consisting of 10 nm of Ca and 150 nm of aluminum, was thermally deposited onto the active layer. The active area of the device was 9 mm^2 for each cell. Current density−voltage (*J*−*V*) characteristics were measured by a computer-controlled Keithley 2602 source measurement unit in the dark and under AM 1.5 illumination conditions, 100 mW/cm^2. All measurements were performed under an ambient atmosphere at room temperature.

Synthesis of Copolymer PBT. To a mixture of compound **1a** (311 mg, 0.5 mmol), 2,5-dibromothiophene (121 mg, 0.5 mmol), 25 mg of $Pd(PPh_3)_2Cl_2$, 5 mg of CuI, and 10 mL of THF was added 5 mL of triethylamine at room temperature. The mixture was purged by N_2 for 10 min and then stirred for 48 h at 60 °C. After that, the solvents were removed in vacuo. The residue was dropped into 50 mL of methanol and filtered. After washing with methanol and acetone, sequentially, for 48 h in a Soxhlet apparatus to remove oligomers and catalyst residues, a red solid was obtained. Yield: 90%. ^1H NMR: 7.34 (br, 2H), 3.60 (br, 16H), 1.72 (br, 16H), 1.33 (br, 48H), 0.86 (br, 24H). ^{13}C NMR: 163.08, 144.65, 144.56, 133.16, 132.85, 124.69, 123.33, 116.12, 93.38, 77.42, 76.58, 50.04, 31.50, 28.43, 28.36, 26.15, 22.58, 13.99.

Synthesis of Copolymer PBB. By following the similar methods, PBB was synthesized with monomers **1a** and 4,7-dibromobenzo-[*c*][1,2,5]thiadiazole. The final product as a black solid was obtained. Yield: 87%. ^1H NMR: 8.13 (br, 2H), 3.73 (br, 24H), 1.79 (br, 24H), 1.35 (br, 72H), 0.87 (br, 36H). ^{13}C NMR: 163.16, 154.19, 146.32, 145.29, 116.45, 116.22, 77.43, 76.58, 62.79, 50.51, 50.17, 49.95, 31.61, 28.56, 26.26, 22.59, 13.99.

Synthesis of Copolymer PBP. By following the similar methods, PBP was synthesized with monomers **1a** and 3,6-dibromo-9-phenyl-9*H*-carbazole. The final product as a red solid was obtained. Yield: 70%. ^1H NMR: 7.60 (br, 4H), 7.52 (br, 7H), 3.80 (br, 60H), 1.73 (br, 60H), 1.33 (br, 180H), 0.87 (br, 90H). ^{13}C NMR: 180.32, 168.30, 154.27, 125.69, 77.42, 76.58, 31.51, 28.43, 26.07, 22.57, 13.98.

Results and Discussion

Synthesis and Characterization of the Copolymers. As illustrated in Scheme 1, the BDF precursor **1a** can readily be copolymerized with three corresponding π-conjugated comonomers to afford the desired copolymers PBT, PBB, and PBP in good yields. All of them were purified by Soxhlet extraction with methanol and acetone and satisfactorily characterized by GPC, NMR, TGA, powder X-ray diffraction (XRD), UV−vis spectroscopy, and electrochemical cyclic voltammetry.

The introduction of hexyl groups renders the copolymers quite soluble in organic solvents such as dichloromethane, chloroform, chlorobenzene, dichlorobenzene, and THF. Moreover, PBT and PBP exhibit a better solubility in dichloromethane than PBB. As shown in Table 1, the weight-average molecular

Table 1. Polymerization Results as Well as Thermal and Optical Properties of the Polymers

polymer	M_w ($\times 10^4$, g/mol)	PDI[a]	BDF:Ar[b]	T_d[c] (°C)	UV−vis (nm) in solution[d]	UV−vis (nm) in film[e]	PL[f] (nm)
PBT	1.8	2.0	2:1	317	276, 421, 511	270, 426, 535	551
PBB	1.6	2.6	3:1	298	281, 460, 566	276, 477, 611	662
PBP	1.5	1.9	7:1	296	276, 410, 487	270, 393, 496	571

[a] Calculated from GPC (eluent: THF; polystyrene standards). [b] Estimated by ^{1}H NMR measurement. [c] Temperature at 5% weight loss by a heating rate of 5 °C/min under nitrogen. [d] Measured in $CHCl_3$ solution (10^{-6} M). [e] Polymer film cast from chloroform solution. [f] Measured in $CHCl_3$ solution (10^{-7} M).

Table 2. Electrochemical Properties, Energy Gaps, XRD Results, and Photovoltaic Properties of the Polymers

polymer	HOMO[a] (eV)	LUMO[a] (eV)	E_g^{el} (eV)	E_g^{opt} (eV)	d_1[b] (Å)	d_2[b] (Å)	J_{sc} (mA/cm^2)	V_{oc} (V)	PCE (%)	FF (%)
PBT	−5.06	−3.20	1.86	1.98	16.2	4.1	3.10	0.53	0.59	35
PBB	−5.25	−3.61	1.64	1.71	17.9	4.1	3.74	0.45	0.53	31
PBP	−5.18	−3.36	1.82	2.01	16.1	4.4	2.19	0.29	0.17	27

[a] The HOMO and LUMO levels were calculated from the onset of the oxidation and reduction potentials in cyclovoltammetry, respectively. [b] Calculated by the formula of $2d \sin \theta = \lambda$, in which the data of θ angles were measured by powder X-ray diffraction.

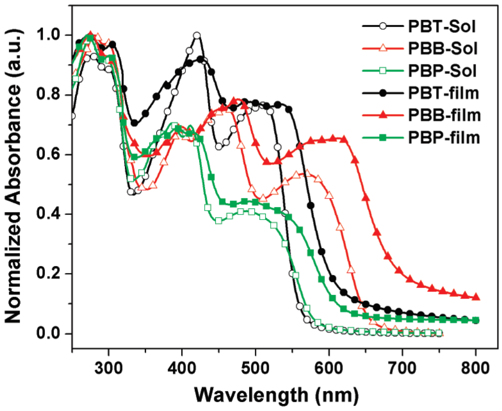


Figure 2. Normalized absorption spectra of the copolymers in $CHCl_3$ and thin films.

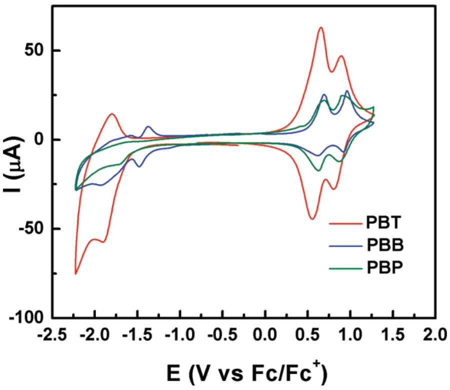


Figure 3. Cyclic voltammograms of the freshly prepared drop-cast films of the copolymers on a polycrystalline Pt bead in CH_3CN. Supporting electrolyte $TBAPF_6$ 0.1 M; scan rate 100 mV s^{-1}.

weights (M_w) and the polydispersity indexes (PDI) of the obtained copolymers appear to be in the range of 15 000−18 000 g/mol and 1.9−2.6, respectively, with reference to polystyrene standards. Estimated by ^{1}H NMR measurements, the ratios of the BDF monomer and the corresponding dibromo comonomers in the polymer chains are 2:1/3:1/7:1 for PBT/PBB/PBP, respectively, which can be accounted for a strong self-coupling of monomer **1a**. The thermal stabilities of these copolymers were examined by thermogravimetric analysis (TGA) (Figure S1 in the Supporting Information); all of them are thermally stable up to 296−317 °C, whereas neither phase transition temperatures nor melting peaks were observed by differential scanning calorimetry (DSC).

Photophysical Properties. The normalized optical absorption spectra of the copolymers in $CHCl_3$ solution and thin films are shown in Figure 2, and the results are listed in Table 1. All copolymers cover broad absorption ranges from the UV to the visible region with high extinction coefficients (Figure S2 in Supporting Information), thus in favor of ligh-harvesting and photocurrent generation. By comparison with an analogous conjugated trimeric unit, namely Ar−≡−BDF−≡−Ar (Ar = pyridine),[9] the lowest energy absorptions within the 500−580 nm region can be interpreted to be HOMO to LUMO type transitions with a substantial intrachain charge transfer (ICT) characteristic (BDF to Ar). As expected, they are bathochromically shifted in thin films, evident by the intense red/black color of the copolymers. The optical band gaps (E_g^{opt}, Table 2) of the three copolymers estimated from the onset absorptions in the films are 1.98, 1.71, and 2.01 eV for PBT, PBB and PBP, respectively. Clearly, the photophysical properties and energy levels of the resultant copolymers can be easily tuned by simply incorporating different electron-withdrawing or -donating comonomers. Furthermore, copolymers PBT, PBB, and PBP emit yellow, orange, and red in $CHCl_3$, respectively (Table 1 and Figure S3 in the Supporting Information), whereas in all cases the emission is quenched in the solid state.

Electrochemical Properties. As depicted in Figure 3, these copolymers in thin films undergo two well-resolved reversible oxidation processes for the oxidation of the BDF units. The oxidation potentials of copolymer PBT are slightly lower than those of two other copolymers while PBT only shows a quasi-reversible reduction wave, suggesting that PBT appears to be more suitable as a p-type transporting material. In contrast, PBB undergoes one reversible and one irreversible reduction process. It can therefore be deduced that PBB containing electron-donating BDF and electron-accepting benzothiadiazole moieties might be both p-type and n-type materials.[10] In PBP, only one irreversible reduction wave was observed. The moderate onset reduction/oxidation potentials of these copolymers PBT, PBB, and PBP were observed at −1.60/0.26, −1.19/0.45, and −1.44/0.38 V, respectively, from which the ionization potentials (IP, HOMO levels) of 5.06−5.25 eV and electron affinities (EA, LUMO levels) of 3.20−3.61 eV were calculated according to the following equation: $E_{HOMO}/E_{LUMO} = [-e(E_{onset} + 4.8)]$ eV, where 4.8 eV is the energy level of ferrocene below the vacuum level.[7,11] Obviously, all of the copolymers have a LUMO level above −4.0 eV, and thus the offsets between the LUMO levels of these copolymers and PCBM (−4.3 eV)[12] are larger than 0.3 eV, indicating that charge transfer from the polymers to PCBM would be efficient.[5b] It is worthwhile to note that electrochemical band gaps (E_g^{el} = IP − EA, in Table 2) of the copolymers are apparently varied when

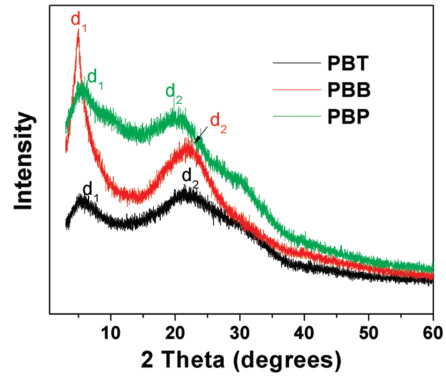


Figure 4. X-ray powder diffraction patterns of the copolymers.

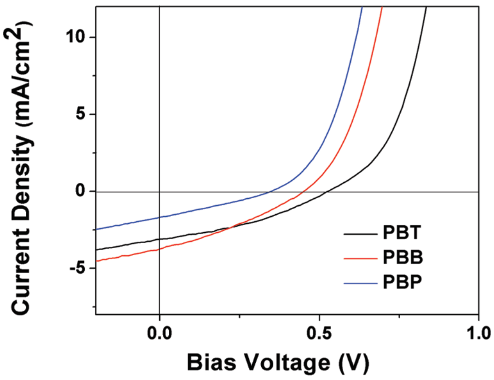


Figure 5. Current density$-$voltage characteristics of devices based on the copolymers/PCBM under AM 1.5 illumination conditions, 100 mW/cm^2.

diverse numbers of the BDF monomer **1a** and different comonomer units are incorporated into the molecular structures. The electrochemical HOMO$-$LUMO gaps correspond also fairly well with the optically determined ones (E_g^{opt}).

X-ray Diffraction. To gain insight into the structural order of the copolymers, powder X-ray diffraction (XRD) analyses were performed. Figure 4 exhibits the XRD curves for the powdery copolymers PBT, PBB, and PBP, and the corresponding d-values are listed in Table 2. All three powder compounds show a typical diffraction pattern characteristic for π-conjugated aromatic polymers that have long side chains: a first diffraction peak appears in the low-angle region at $2\theta = 4.95°-5.5°$ and a second one around $2\theta = 19.95°-21.75°$. The low-angle peaks with corresponding d_1 values between 16 and 18 Å are assigned to the interchain spacing between polymer main chains, where the alkyl substituents are segregated as reported for analogous polymers.[13] This range of d_1 values is reasonable for the pending hexyl substituents; however, the variation of the peak width, which is a function of the degree of crystallinity, cannot be explained at this stage. The broad peaks in the wide-angle region correspond to d_2 values between 4.1 and 4.4 Å, and it is reasonable to assign them to the distance between disordered alkyl chains, although the peaks may also contain contributions from a face-to-face packing of the polymer planes.[13a,b,14]

Organic Photovoltaic Cell Properties. The bulk heterojunction PSCs were fabricated with a device structure of ITO/PEDOT:PSS/polymer:PCBM (1:4, w/w)/Ca/Al. Figure 5 shows the $I-V$ curves of the devices under the illumination of AM 1.5, 100 mW/cm^2. The photovoltaic parameters, including the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), and power conversion efficiency (PCE), are summarized in Table 2. The sequence of the PCE values for PBT, PBB, and PBP are obtained according to their V_{oc} values of 0.53, 0.45, and 0.29 V, respectively. Notably, the device containing PBB has a highest J_{sc} value of 3.74 mA/cm^2, very probably due to the lowest optical band gap together with the strong and broad absorption spectrum (Figure 2). It has been demonstrated that the V_{oc} value in BHJ solar cells is linearly dependent on the difference between the HOMO level of p-type polymer and the LUMO level of an n-type PCBM.[2] However, it turns out that the V_{oc} value of the cell device based on PBT (HOMO energy level: -5.06 eV) is higher than those containing PBB (-5.25 eV) and PBP (-5.18 eV). Apparently, this disparity is a result of the electronic properties of the donor, acceptor, and the D/A interface, specifically carrier recombination, degree of phase-separation between the components in the blend, the photoinduced dipole formed at the interface due to the charge transfer, and the surface morphology of the active layers of polymer:PCBM.[15] All these factors must be taken into account, which can modify the energetically expected V_{oc} value. Although preliminary studies on BHJ cells fabricated by blended BDF-based copolymers show the best performance only with the maximum PCE value of 0.59%, fascinating features of BDF derivatives that include an electron-rich π-system, structural planarity, and intrinsic optical properties make them very appealing in this field. To improve the cell performance, on one hand, it is desirable to prepare alternating D$-$A copolymers with a well-defined structure leading to the formation of an interpenetrating network with the optimal morphology for the good control of charge separation and transport. Because of the electron-withdrawing effect of the acceptor units, the resulting copolymers are expected to show a low band gap, but a precise control of HOMO and LUMO levels to their optimal values is still challenging. On the other hand, optimal device fabrication conditions such as the appropriate ratio of the polymer to PCBM, and/or controlling the phase morphology by processing additives or solvent annealing, also play a vital role.

Conclusions

In summary, a series of benzodifuran-based copolymers have been synthesized and characterized. These copolymers appear promising for the application in BHJ solar cells due to their good solubilities and high thermal stabilities as well as their low band gaps. It has been demonstrated that their electronic and photovoltaic properties can be easily tuned by incorporating different comonomers into the polymer backbone in different ratios. The preliminary investigation on the photovoltaic device based on a PBT:PCBM bulk heterojunction gives a PCE value of 0.59%. Deeper investigations for better photovoltaic properties are currently in progress by the rational design and synthesis of BDF-based copolymers and simultaneously by optimizing the fabrication conditions to achieve high-performance BHJ solar cells.

Acknowledgment. This work was supported by the Swiss National Science Foundation (Grant Nos. 200020-116003, 200020-130266/1, 200020-117572, and 200021-124643) and EU-(FUNMOLS FP7-212942-1) as well as the NCCR Nanosciences and National Nature Science Foundation of China (No. 50973092).

Supporting Information Available: ^{1}H NMR spectra of all copolymers; TGA, UV$-$vis, and PL spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Ahmed, E.; Kim, F. S.; Xin, H.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 8615–8618. (b) Delgado, J. L.; Bouit, P.-A.; Filippone, S.; Herranz, M. A.; Martín, N. *Chem. Commun.* **2010**, *46*, 4853–4865.

(c) Zhou, E.; Nakamura, M.; Nishizawa, T.; Zhang, Y.; Wei, Q.; Tajima, K.; Yang, C.; Hashimoto, K. *Macromolecules* **2008**, *41*, 8302–8305.

(2) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868–5923.

(3) (a) Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Aích, B. R.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, *132*, 5330–5331. (b) Li, Y. F.; Zou, Y. P. *Adv. Mater.* **2008**, *20*, 2952–2958.

(4) (a) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894–12895. (b) Wei, H. Y.; Huang, J. H.; Ho, K. C.; Chu, C. W. *Appl. Mater. Interfaces* **2010**, *2*, 1281–1285. (c) Barrau, S.; Andersson, V.; Zhang, F.; Masich, S.; Bijleveld, J.; Andersson, M. R.; Inganäs, O. *Macromolecules* **2009**, *42*, 4646–4650. (d) Kietzke, T.; Hörhold, H. H.; Neher, D. *Chem. Mater.* **2005**, *17*, 6532–6537. (e) Chen, H.; Huang, H.; Tian, Z.; Shen, P.; Zhao, B.; Tan, S. *Eur. Polym. J.* **2010**, *46*, 673–680.

(5) (a) Huo, L.; Hou, J.; Zhang, S.; Chen, H. Y.; Yang, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 1–5. (b) Chen, H. Y.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. *Nature Photonics* **2009**, *3*, 649–653. (c) Huo, L.; Hou, J.; Zhang, S.; Chen, H. Y.; Yang, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 1500–1503. (d) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv. Mater.* **2010**, *22*, 1–4.

(6) Liang, Y.; Wu, Y.; Feng, D.; Tsai, S. T.; Son, H. J.; Li, G.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 56–57.

(7) Liang, Y.; Feng, D.; Wu, Y.; Tsai, S. T.; Li, G.; Ray, C.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 7792–7799.

(8) (a) Tsuji, H.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 11902–11903. (b) Tsuji, H.; Mitsui, C.; Sato, Y.; Nakamura, E. *Adv. Mater.* **2009**, *21*, 3776–3779. (c) Nakano, K.; Takahashi, M.; Kawaguchi, K.; Nozaki, K. *Synth. Met.* **2009**, *159*, 939–942.

(9) Yi, C.; Blum, C.; Lehmann, M.; Keller, S.; Liu, S.-X.; Frei, G.; Neels, A.; Hauser, J.; Schürch, S.; Decurtins, S. *J. Org. Chem.* **2010**, *75*, 3350–3357.

(10) Li, K.-C.; Huang, J.-H.; Hsu, Y.-C.; Huang, P.-J.; Chu, C.-W.; Lin, J.-T.; Ho, K.-C.; Wei, K.-H.; Lin, H.-C. *Macromolecules* **2009**, *42*, 3681–3693.

(11) (a) Chen, C. P.; Chan, S. H.; Chao, T. C.; Ting, C.; Ko, B. T. *J. Am. Chem. Soc.* **2008**, *130*, 12828–12833. (b) Zhou, E.; Wei, Q.; Yamakawa, S.; Zhang, Y.; Tajima, K.; Yang, C.; Hashimoto, K. *Macromolecules* **2010**, *43*, 821–826.

(12) (a) Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. *Adv. Mater.* **2006**, *18*, 789–794. (b) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15–26. (c) Chen, C. P.; Chan, S. H.; Chao, T. C.; Ting, C.; Ko, B. T. *J. Am. Chem. Soc.* **2008**, *130*, 12828–12833. (d) Wang, E.; Wang, M.; Wang, L.; Duan, C.; Zhang, J.; Cai, W.; He, C.; Wu, H.; Cao, Y. *Macromolecules* **2009**, *42*, 4410–4415.

(13) (a) Yamamoto, T.; Lee, B. L. *Macromolecules* **2002**, *35*, 2993–2999. (b) Li, K. C.; Huang, J. H.; Hsu, Y. C.; Huang, P. J.; Chu, C. W.; Lin, J. T.; Ho, K. C.; Wei, K. H.; Lin, H. C. *Macromolecules* **2009**, *42*, 3681–3693. (c) Yamamoto, T.; Arai, M.; Kokubo, H. *Macromolecules* **2003**, *36*, 7986–7993. (d) Qin, R.; Li, W.; Li, C.; Du, C.; Veit, C.; Schleiermacher, H. F.; Andersson, M.; Bo, Z.; Liu, Z.; Inganas, O.; Wuerfel, U.; Zhang, F. *J. Am. Chem. Soc.* **2009**, *131*, 14612–14613. (e) Wu, P. T.; Ren, G.; Jenekhe, S. A. *Macromolecules* **2010**, *43*, 3306–3313. (f) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, B.; Neagu-Plesu, R.; Belletête, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2008**, *130*, 732–742.

(14) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.-L.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047–2048.

(15) (a) Perez, M. D.; Borek, C.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2009**, *131*, 9281–9286. (b) Chen, H.; Huang, H.; Tian, Z.; Shen, P.; Zhao, B.; Tan, S. *Eur. Polym. J.* **2010**, *46*, 673–680. (c) Winder, C.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 1077–1086.