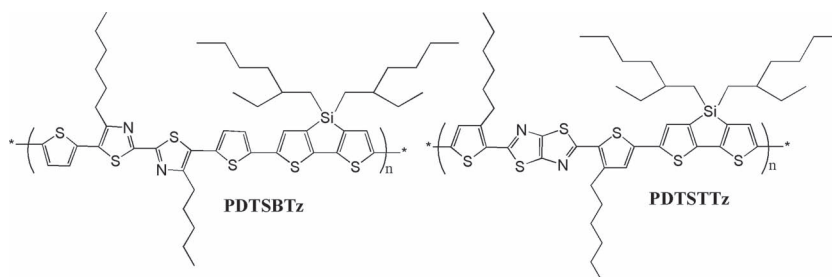


Synthesis and Characterization of a Copolymer Based on Thiazolothiazole and Dithienosilole for Polymer Solar Cells

Maojie Zhang, Xia Guo, and Yongfang Li*

In recent years, polymer solar cells (PSCs) have attracted considerable attention because of their advantages of low cost, easy fabrication, light weight, and the capability to fabricate flexible large-area devices.^[1–5] The key issue in studies of PSCs is the power conversion efficiency (PCE) of the devices. The factors that determine the PCE of the PSCs are the open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and fill factor (FF). V_{OC} is limited by the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.^[6] The J_{SC} is closely related to the absorption capacity and charge-carrier mobility of the photo-voltaic materials, and the FF is influenced by the charge-carrier mobility of the photoactive layer. Higher charge-carrier mobility results in larger J_{SC} and higher FF values.^[7] The photoactive layer of PSCs is commonly composed of a blend of a conjugated polymer donor and a fullerene derivative acceptor such as [6,6]-phenyl- C_{60} -butyric acid methyl ester (PC₆₀BM) or [6,6]-phenyl- C_{70} -butyric acid methyl ester (PC₇₀BM). Regioregular poly(3-hexylthiophene) (P3HT) and PC₆₀BM are the most representative donor and acceptor materials, and the PCE values of PSCs based on P3HT/PCBM can reach over 4%.^[8] Nevertheless, the relatively large bandgap and higher-lying HOMO energy level (−4.76 eV)^[9] of P3HT significantly limits the J_{SC} and V_{OC} values (V_{OC} is limited to ca. 0.6 V) of PSCs based on P3HT/PCBM. In order to improve the visible absorption and decrease the HOMO energy level of conjugated polymers, design and synthesis of donor–acceptor (D–A) copolymers has been proven to be the most successful strategy.^[10–17] With this strategy, the PCE of the PSCs using new D–A copolymers as donor materials has recently reached up to 6–7%.^[16,17]

In our previous work, we synthesized a D–A copolymer **PDTSBTz** (see Scheme 1) based on a dithienosilole (DTS) donor unit and a bithiazole (BTz) acceptor.^[18] **PDTSBTz** (**P3** in reference [18]) exhibited a hole mobility of $3.07 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$



Scheme 1. Molecular structures of **PDTSBTz** and **PDTSTTz**.

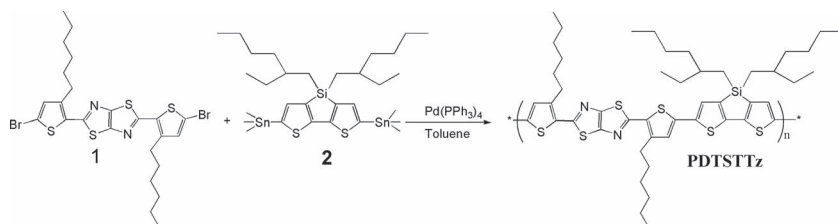
and PCE of 2.86% when used as a donor blended with PC₇₀BM as an acceptor.^[18] Compared with bithiazole, thiazolothiazole (TTz) has a rigid and coplanar fused ring and ensures a highly extended π -electron system and strong π stacking. Therefore, the TTz unit has attracted much interest in the construction of high-performance organic/polymer semiconductors and for applications in optoelectronic devices.^[19–24] The field-effect hole mobility of a conjugated polymer containing TTz and thiophene oligomer units in the polymer main chain has been reported to reach as high as $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[19] The PSCs based on a D–A copolymer of TTz and carbazole exhibit a high PCE of 4.88%.^[24] Based on previous reports, if we replace bithiazole with thiazolothiazole in **PDTSBTz**, we could improve its hole mobility and further improve its photovoltaic performance. Using this consideration, we synthesized a new D–A copolymer, **PDTSTTz** (see Scheme 1), based on DTS as the donor unit and TTz as the acceptor. In comparison with **PDTSBTz**, the two hexyl substituents on bithiazole unit are moved to the two thiophene units in **PDTSTTz**, maintaining the good solubility of the polymer. **PDTSTTz** indeed exhibited a high hole mobility of $3.56 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, one order of magnitude higher than that of **PDTSBTz**. Additionally, the polymer possesses a relatively higher-lying HOMO energy level of −5.06 eV. The PCE of the PSCs based on **PDTSTTz**:PC₇₀BM = 1:1 (w/w) reached 5.59% with V_{OC} of 0.77 V, a J_{SC} of 11.9 mA cm^{-2} , and a FF of 61%, under the illumination of AM1.5, 100 mW cm^{-2} . The larger J_{SC} and higher FF in comparison with those of **PDTSBTz**^[18] should benefit from the higher hole mobility of **PDTSTTz**. The results indicate that **PDTSTTz** is a promising high performance photovoltaic donor material for PSCs.

PDTSTTz was synthesized via a Stille coupling reaction using $\text{Pd(PPh}_3)_4$ as the catalyst, as shown in Scheme 2. The copolymer has good solubility in common organic solvents such as chloroform, toluene, chlorobenzene, etc. The number-average molecular weight (M_n) of **PDTSTTz** is 8.7 kDa with a polydispersity index (PDI) of 1.59.

M. Zhang, X. Guo, Prof. Y. Li
Beijing National Laboratory for Molecular Sciences
CAS Key Laboratory of Organic Solids
Institute of Chemistry
Chinese Academy of Sciences
Beijing 100190, China
E-mail: liyf@iccas.ac.cn

M. Zhang
Graduate University of Chinese Academy of Sciences
Beijing 100049, China

DOI: 10.1002/aenm.201100193



Scheme 2. Synthetic route to PDTSTTz.

The thermal stability of the polymer was investigated with thermogravimetric analysis (TGA). The TGA result (Supporting Information (SI), Figure S1) reveals that the onset temperature with 5% weight-loss (T_d) of PDTSTTz is 338 °C. This indicates that the thermal stability of PDTSTTz is good for optoelectronic device applications.

Figure 1 shows the UV-vis absorption spectra of dilute polymer solutions in chloroform and films spin-coated onto quartz substrates. The absorption spectra of the PDTSTTz^[18] solution and film are also shown in Figure 1 for clear comparison. In CHCl₃ solution, the spectrum of PDTSTTz showed an absorption maximum (λ_{max}) of 560 nm, which was red-shifted by ca. 50 nm compared with that of PDTSTz (510 nm). The absorption maximum of PDTSTTz film is at 605 nm, which is red-shifted by ca. 20 nm in comparison with that of PDTSTz film. These results indicate that introducing the thiazolothiazole unit instead of a bithiazole unit to the main chain of the polymer extends the conjugation length and red-shifts the absorption. The absorption edges (λ_{edge}) of PDTSTTz film was 685 nm, with an optical bandgap (E_g^{opt}) of 1.81 eV, which is slightly smaller than that of PDTSTz (1.85 eV).^[18]

Cyclic voltammetry was performed to determine the HOMO and LUMO energy levels of the conjugated polymers.^[25] As shown in the cyclic voltammogram of PDTSTTz (see Figure 2), the onset reduction potential (ϕ_{red}) is -1.90 V versus Ag/Ag⁺, and the onset oxidation potential (ϕ_{ox}) is 0.36 V versus Ag/Ag⁺. The HOMO and LUMO energy levels as well as the electrochemical band gap (E_g^{EC}) of the polymer are -5.06 eV, -2.81 eV

and 2.26 eV, respectively, calculated from ϕ_{ox} and ϕ_{red} .^[26] The HOMO energy level of the polymer is significantly deeper than that (-4.76 eV)^[9] of P3HT. The deeper HOMO level at -5.06 eV for the polymer implies that the polymer could be more stable against oxidation, which will enhance the device stability. And the deeper HOMO level is beneficial to a higher V_{OC} for the PSCs with the polymer as donor, since V_{OC} of PSCs is related to the difference of the LUMO of the

acceptor and the HOMO of the donor.^[20]

The hole mobility of PDTSTTz was measured to be $3.56 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, by the space-charge-limited current (SCLC) method (see SI), which is one order of magnitude higher than that of PDTSTz ($3.07 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[18] The higher mobility of PDTSTTz could be benefitted from the more rigid and coplanar backbone and stronger intermolecular interaction caused by thiazolothiazole unit in the polymer. The higher hole mobility of PDTSTTz is desirable for the application as photovoltaic donor materials in PSCs.

Photovoltaic properties of PDTSTTz were investigated by fabricating the PSCs based on PDTSTTz as donor and PC₇₀BM as acceptor with the device structure of ITO/PEDOT: PSS/PDTSTTz:PC₇₀BM/Ca/Al. Figure 3 shows the current density-voltage characteristic of the device under the illumination of AM1.5, 100 mW cm⁻², and Table 1 lists the photovoltaic performances of the PSCs based on PDTSTTz or PDTSTz as donor and PC₇₀BM as acceptor. The PSC based on PDTSTTz:PC₇₀BM = 1:1 (w/w) demonstrated a V_{OC} of 0.76 V, J_{SC} of 10.5 mA cm⁻², and a FF of 0.587, leading to a PCE of 4.68%. J_{SC} of the device based on PDTSTTz increased by ca. 34% compared with that of PDTSTz, which should be due to the higher hole mobility and red-shifted absorption of PDTSTTz. After annealing at 100 °C for 15 min, J_{SC} and FF of the device further increased to 11.9 mA cm⁻² and 0.61, respectively, and the PCE reached 5.59%. The slightly lower FF at higher PC₇₀BM content (1:2) could be ascribed to an unbalanced charge transporting

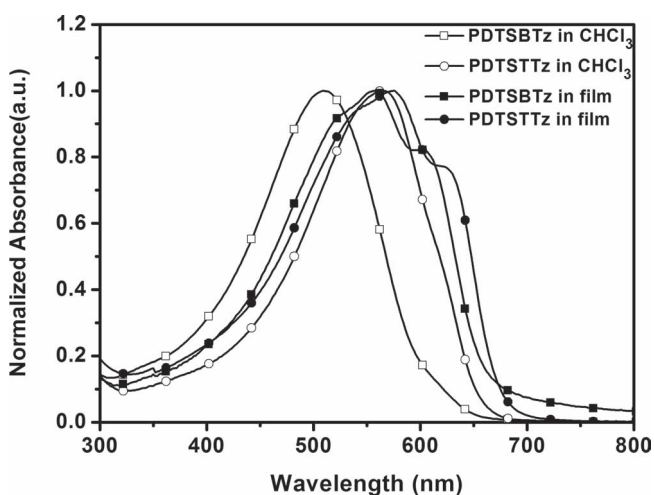


Figure 1. Absorption spectra of PDTSTz and PDTSTTz in chloroform and in the solid state.

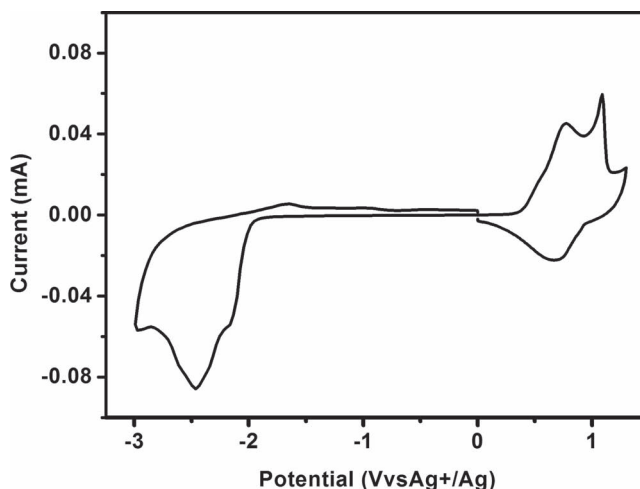


Figure 2. Cyclic voltammogram of a PDTSTTz film on a platinum electrode measured in 0.1 mol L⁻¹ Bu₄NPF₆ acetonitrile solutions at a scan rate of 100 mV s⁻¹.

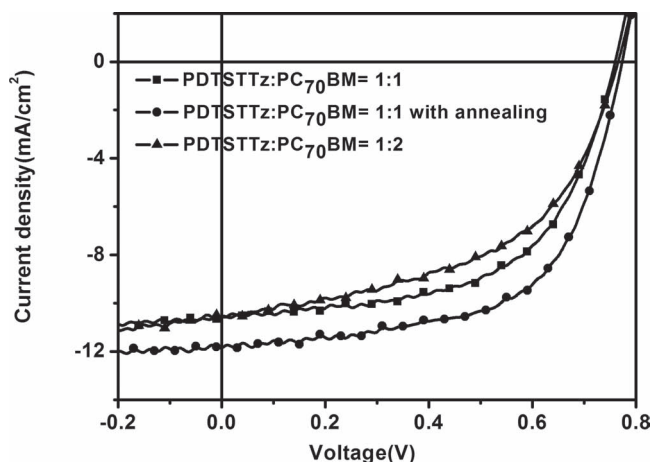


Figure 3. I - V curves of the polymer solar cells based on PDTSTTz:PC₇₀BM under the illumination of AM 1.5, 100 mW cm⁻².

properties between holes and electrons due to the high PC₇₀BM content.^[27]

The external quantum efficiency (EQE) of the PSCs based on PDTSTTz:PC₇₀BM (1:1 w/w) with and without annealing are shown in Figure 4. The EQE curve of the PSC based on PDTSTTz:PC₇₀BM = 1:1 without thermal annealing covers a broad wavelength range from 350 to 700 nm with the maximum EQE value of 64.2% at ca. 560 nm. With annealing at 100 °C for 15 min, the EQE values increased in the whole wavelength range and the maximum EQE value increased up to 71.3%, which is in agreement with the J_{SC} increasement of the PSC with annealing.

The morphology of the blend film of PDTSTTz and PC₇₀BM with or without annealing was observed by atomic force microscopy (AFM), as shown in Figure 5. After annealing at 100 °C for 15 min, the film shows smaller roughness with an average roughness (R_a) of 1.56 nm and more smooth surface, in comparison with that (2.20 nm) of the film before annealing. The results indicate that the improvement of PCE after annealing could be ascribed to the morphology improvement by the annealing.

In conclusion, we have synthesized a new D-A copolymer (PDTSTTz) containing a dithienosilole donor unit and a thiazolothiazole acceptor unit, by the Pd-catalyzed Stille-coupling method. PDTSTTz film shows broader absorption in the wavelength range of 400–685 nm, and possesses a lower-lying HOMO energy level at -5.06 eV and a higher hole mobility of 3.56×10^{-3} cm² V⁻¹ s⁻¹. The PCE of the PSC based on PDTSTTz:PC₇₀BM (1:1, w/w) reached 4.68% with $J_{SC} = 10.5$ mA cm⁻², $V_{OC} = 0.76$ V,

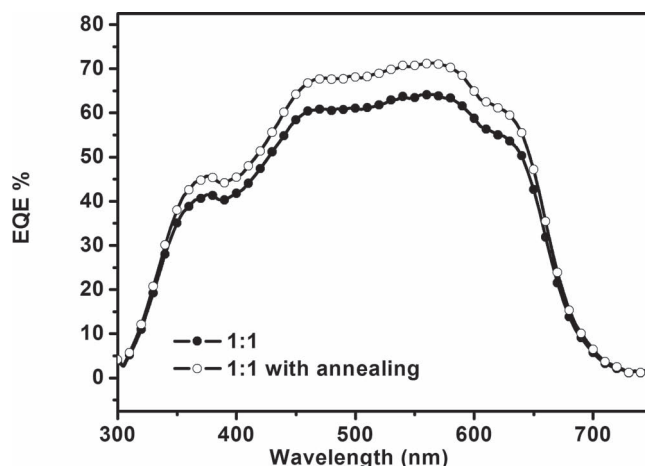


Figure 4. EQE of the PSCs based on PDTSTTz:PC₇₀BM (1:1 w/w) with and without annealing.

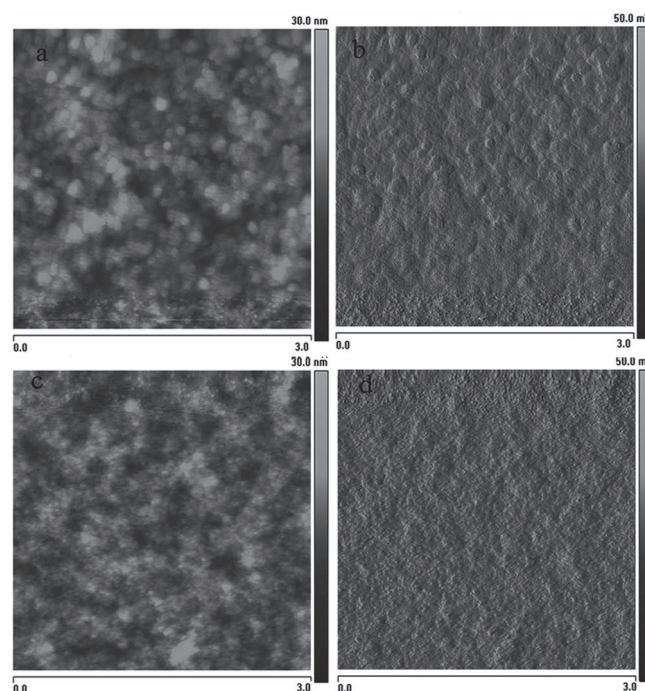


Figure 5. AFM topography images (a,c) and phase contrast images (b,d) of PDTSTTz:PC₇₀BM (1:1) films: without annealing (a,b), after annealing at 100 °C for 15 min (c,d).

and FF = 0.587, under the illumination of AM1.5, 100 mW cm⁻². After annealing at 100 °C for 15 min, the PCE increased to 5.59% with $J_{SC} = 11.9$ mA cm⁻², $V_{OC} = 0.77$ V, and FF = 0.61. These results indicate that PDTSTTz is a promising high-performance donor material for application in PSCs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors. SI includes an Experimental Section, TGA, and hole mobility measurements.

Table 1. Photovoltaic performances of the PSCs based on PDTSTTz or PDTSTBz as donor and PC₇₀BM as acceptor.

	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF	PCE [%]
PDTSTTz:PC ₇₀ BM = 1:1 ^{a)}	0.76	10.5	0.587	4.68
PDTSTTz:PC ₇₀ BM = 1:1 ^{b)}	0.77	11.9	0.61	5.59
PDTSTTz:PC ₇₀ BM = 1:2 ^{a)}	0.77	10.57	0.514	4.18
PDTSTBz:PC ₇₀ BM = 1:1 ^{c)}	0.68	7.85	0.535	2.86

^{a)}without annealing; ^{b)}after annealing at 100 °C for 15 min; ^{c)}data from reference [18].

Acknowledgements

This work was supported by NSFC (Nos. 20874106, 20821120293, and 50933003), The Ministry of Science and Technology of China (No: 2010DFA64680), and Chinese Academy of Sciences (KGCX2-YW-399+9-1).

Received: April 9, 2011

Published online: May 17, 2011

- [1] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, 270, 1789.
- [2] a) H.-Y. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu, G. Li, *Nat. Photonics* **2009**, 3, 649; b) Y. Y. Liang, Z. Xu, J. B. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. P. Yu, *Adv. Mater.* **2010**, 22, E135.
- [3] a) J. W. Chen, Y. Cao, *Acc. Chem. Res.* **2009**, 42, 1709; b) G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **2009**, 21, 1323; c) Y.-J. Chen, S.-H. Yang, C.-S. Hsu, *Chem. Rev.* **2009**, 109, 5868; d) Y. F. Li, Y. P. Zou, *Adv. Mater.* **2008**, 20, 2952.
- [4] B. C. Thompson, J. M. J. Fréchet, *Angew. Chem. Int. Ed.* **2008**, 47, 58.
- [5] S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. H. Lee, A. J. Heeger, *Nat. Photonics* **2009**, 3, 297.
- [6] G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf, C. J. Brabec, *Adv. Mater.* **2008**, 20, 579.
- [7] Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L. Yu, *J. Am. Chem. Soc.* **2009**, 131, 56.
- [8] a) G. Li, V. Shrotriva, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* **2005**, 4, 864; b) W. L. Ma, C. Y. Yang, X. Gong, K. Lee, A. J. Heeger, *Adv. Funct. Mater.* **2005**, 15, 1617.
- [9] J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang, Y. F. Li, *J. Am. Chem. Soc.* **2006**, 128, 4911.
- [10] a) D. Mühlbacher, M. Scharber, M. Morana, Z. G. Zhu, D. Waller, R. Gaudiana, C. J. Brabec, *Adv. Mater.* **2006**, 18, 2884; b) Z. Zhu, D. Waller, R. Gaudiana, M. Morana, D. Mühlbacher, M. Scharber, C. J. Brabec, *Macromolecules* **2007**, 40, 1981; c) M. Svensson, F. L. Zhang, S. C. Veenstra, W. J. H. Verhees, J. C. Hummelen, J. M. Kroon, O. Inganäs, M. R. Andersson, *Adv. Mater.* **2003**, 15, 988.
- [11] a) E. G. Wang, L. Wang, L. F. Lan, C. Luo, W. L. Zhuang, J. B. Peng, Y. Cao, *Appl. Phys. Lett.* **2008**, 92, 033307; b) Y. J. Xia, X. Y. Deng, L. Wang, X. Z. Li, X. H. Zhu, Y. Cao, *Macromol. Rapid Commun.* **2006**, 27, 1260.
- [12] a) N. Blouin, A. Michaud, M. Leclerc, *Adv. Mater.* **2007**, 19, 2295; b) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletete, G. Durocher, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.* **2008**, 130, 732; c) Y. P. Zou, A. Najari, P. Berrouard, S. Beaupré, B. R. Aich, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.* **2010**, 132, 5330.
- [13] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, *Nat. Mater.* **2007**, 6, 497.
- [14] J. H. Hou, H. Y. Chen, S. Q. Zhang, G. Li, Y. Yang, *J. Am. Chem. Soc.* **2008**, 130, 16144.
- [15] a) E. J. Zhou, M. Nakamura, T. Nishizawa, Y. Zhang, Q. S. Wei, K. Tajima, C. H. Yang, K. Hashimoto, *Macromolecules* **2008**, 41, 8302; b) E. J. Zhou, S. Yamakawa, K. Tajima, C. H. Yang, K. Hashimoto, *Chem. Mater.* **2009**, 21, 4055.
- [16] T. Chu, J. Lu, S. Beaupré, Y. Zhang, J. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding, Y. Tao, *J. Am. Chem. Soc.* **2011**, 133, 4250.
- [17] a) H. Zhou, L. Yang, A. Stuart, S. Price, S. Liu, W. You, *Angew. Chem. Int. Ed.* **2011**, 50, 2995; b) S. Price, A. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.* **2011**, 133, 4625.
- [18] M. J. Zhang, H. J. Fan, X. Guo, Y. J. He, Z. G. Zhang, J. Min, J. Zhang, G. J. Zhao, X. W. Zhan, Y. F. Li, *Macromolecules* **2010**, 43, 5706.
- [19] I. Osaka, R. Zhang, G. Sauve, D. M. Smilgies, T. Kowalewski, R. D. McCullough, *J. Am. Chem. Soc.* **2009**, 131, 2521.
- [20] S. Ando, J. I. Nishida, H. Tada, Y. Inoue, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2005**, 127, 5336.
- [21] I. Osaka, R. Zhang, J. Liu, D. Smilgies, T. Kowalewski, R. D. McCullough, *Chem. Mater.* **2010**, 22, 4191.
- [22] I. H. Jung, J. Yu, E. Jeong, J. Kim, S. Kwon, H. Kong, K. Lee, H. Y. Woo, H. K. Shim, *Chem. Eur. J.* **2010**, 16, 3743.
- [23] a) Q. Q. Shi, H. J. Fan, Y. Liu, W. P. Hu, Y. F. Li, X. W. Zhan, *J. Phys. Chem. C* **2010**, 114, 16843; b) M. Yang, B. Peng, B. Liu, Y. P. Zou, K. C. Zhou, Y. H. He, C. Y. Pan, Y. F. Li, *J. Phys. Chem. C* **2010**, 114, 17989.
- [24] S. Lee, J. Cho, Y. Goo, W. Shin, J. Lee, H. Lee, I. Kang, H. Shim, S. Moo, *Chem. Commun.* **2011**, 47, 1791.
- [25] Y. F. Li, Y. Cao, J. Gao, D. L. Wang, G. Yu, A. J. Heeger, *Synth. Met.* **1999**, 99, 243.
- [26] Q. J. Sun, H. Q. Wang, C. H. Yang, Y. F. Li, *J. Mater. Chem.* **2003**, 13, 800.
- [27] J. H. Huang, Z. Y. Ho, D. Kekuda, Y. Chang, C. W. Chu, K. C. Ho, *Nanotechnology* **2009**, 20, 025202.