J|A|C|S
COMMUNICATIONS

Single Microwire Transistors of Oligoarenes by Direct Solution Process

Yan Zhou,† Wen-Jun Liu,† Yuguo Ma,*,† Hailiang Wang,† Limin Qi,*,† Yong Cao,‡ Jian Wang,*,‡ and Jian Pei*,†

Key Laboratories of Bioorganic Chemistry and Molecular Engineering and of Polymer Chemistry and Physics of Ministry of Education, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry, Peking University, Beijing 100871, China, and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, and Key Lab of Specially Functional Materials, Ministry of Education, Guangzhou 510640, China

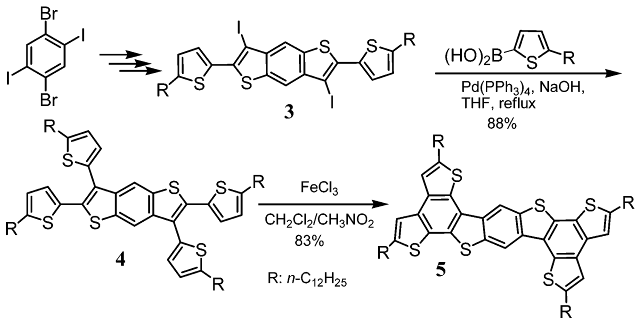
Received July 8, 2007; E-mail: jianpei@pku.edu.cn

Considerable attention has been paid to one-dimensional (1D) nano- or microstructures of organic π-conjugated materials due to their potential applications in organic field-effect transistors (OFETs).[1] Arene derivatives usually form 1D nano- or microstructures by physical vapor transport or substrate-assisted evaporation.[1c,f,2] However, high vacuum and high temperature were required for such physical vapor transport processes in which only some specific molecules could be fabricated. For 1D inorganic nanomaterials, solution processes have been widely applied in devices fabrication due to the convenience and low cost.[3] Such solution processes for OFET utilizing spontaneously self-assembled organic molecules have achieved remarkable advancement very recently.[4] However, during the preparation of the nano- or microwires, solvents with high boiling point were normally involved owing to poor solubility of organic materials. As a result, thermal annealing was required to remove solvents in device fabrication which had adverse effects on the performance of the organic nano- or microwire transistors.[4] Therefore, it is still a challenge to synthesize soluble oligoarenes which could not only easily form 1D structures but also bear the solution process to achieve high mobility.

Among oligoacenes, pentacene with a high measured mobility (1.5 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$) has become a promising material for OFETs.[5] To improve the stability of pentacene, some oligoarenes fused with thiophene units showed remarkable high performance and stability in transistor fabrication under ambient conditions.[6] In this contribution, we report development of a novel planar condensed benzothiophene through a facile approach. We utilized the commercially available 1,4-dibromo-2,5-diiodobenzene as the starting material to produce the final product **5** via five steps in about 38% overall yield. This molecule with alternate benzene and thiophene units combines the elements of oligoacenes and peripherally rich sulfur atoms, which favors $\pi-\pi$ stacking to form 1D nano- or microstructures. The individual microwire transistors with carrier mobility as high as 0.01 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ were easily fabricated utilizing this molecule by direct solution process.

Scheme 1 illustrates the approach to oligoarene **5**. **3** was obtained following the procedure described in our previous contribution.[7] The Suzuki coupling between **3** and 5-dodecylthienyl-2-boronic acid afforded **4** in 88% yield. The oxidative C−C bond formation between two β-positions of thiophene units produced **5** in 83% yield,[8] in which two 1,4,9-trithiatriindene fused the same benzene ring to form a large planar π-system. The long alkyl substituents provided the solubility, the flexibility, and the self-assembled efficiency of **5**.[2a] **5** dissolved in common organic solvents, such as $CHCl_3$ and THF. The structure and purity were confirmed by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF MS, and elemental analysis (see the Supporting Information).

Scheme 1. Synthesis of **5**



The large planar π-conjugated structure favors highly ordered self-assembly by $\pi-\pi$ stacking,[2a] which was evidenced by the concentration-dependent ^1H NMR spectra and the absorption spectra of **5** in solution and in the solid state. The signal at a chemical shift of 8.65 ppm assigned to the proton at the *meso*-benzene ring significantly shifted to 8.27 ppm when the concentration of the $CDCl_3$ solution increased from 1.2 to 60 mg/mL at 55 °C, as shown in Figure 1. It was also observed that other two aryl signals exhibited similar behaviors. Such shifts are a result of shielding from the ring current of neighboring aromatic molecules within a cofacial stack.[9] Figure S2 shows the absorption spectra in CH_2Cl_2 solution (10^{-5} M) and in film coated with microwires. The absorption spectrum of **5** in dilute solution exhibited three major bands with absorption λ_{max} at 312, 369, and 395 nm. After **5** formed the microwires, the peak at 395 nm red-shifted about 19 nm to 414 nm and became the absorption maximum, while the absorption band at 369 nm also red-shifted 19 nm to 388 nm. Such absorption results indicated the effective assembly of **5** through $\pi-\pi$ stacking.[10]

Figure 2A illustrates the SEM image of **5** directly precipitated from 1 mM CH_2Cl_2 solution. **5** showed 1D molecular assembly microwires with a diameter in the range of 500 nm to 1 μm and length about 30−100 μm, which correspond to an aspect ratio of about 60−100. Such 1D morphology strongly indicated the dominant effect of $\pi-\pi$ interactions over that of van der Waals attractions between the alkyl chains.[11] The 1D self-assembly process can be controlled, and some different 1D nano- or microstructures were obtained by utilizing different solvents and substrates as shown in Figure 2B−E. In particular, different self-assembled structures of **5** formed on the Si and SiO_2 surfaces from the *n*-dodecane solution (1 mg/10 mL) under the same process conditions. The broom-like structures were obtained by drop-casting the *n*-dodecane solution of **5** on the silicon wafer while the ribbons with a diameter of 100 nm were obtained on the SiO_2 surface. However, the flower-

---

† Peking University.
‡ South China University of Technology.

10.1021/ja075045f CCC: $37.00 © 2007 American Chemical Society

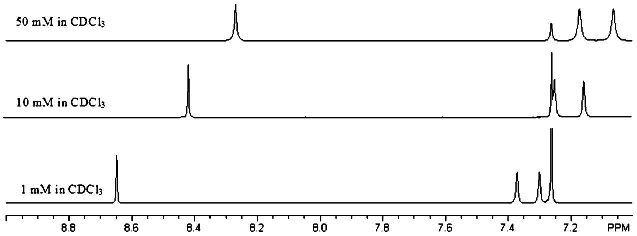


Figure 1. Comparison of ^{1}H NMR spectra of **5** at different concentration.

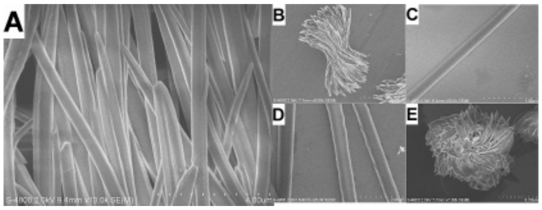


Figure 2. SEM images of **5**: (A) precipitation from CH_2Cl_2 (1 mg/mL); (B) *n*-dodecane solution (1 mg/10 mL) drop-cast on Si wafer; (C) *n*-dodecane solution (1 mg/10 mL) drop-cast on SiO_2; (D) precipitation from THF solution (1 mg/1 mL); (E) THF solution (1 mg/1 mL) drop-cast on Si wafer.

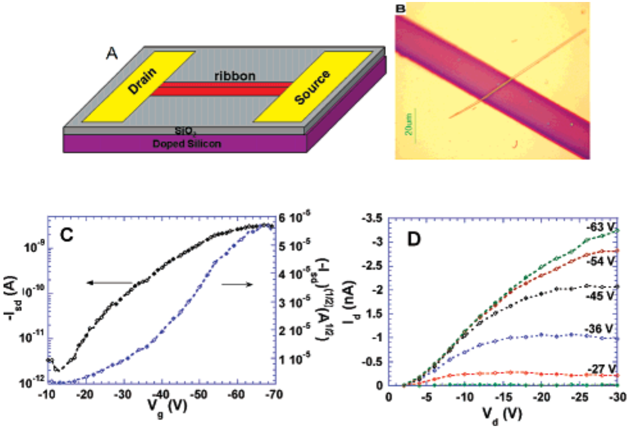


Figure 3. (A) Schematic of a FET from an individual microwire. (B) The microscope image of the individual wire OFET. (C) Transfer characteristics of **5** microwire devices and (D) transistor output. The electrical characteristics correspond to our best performing devices.

like structures were achieved from drop-casting the THF solution of **5** (1 mg/1 mL) on the silicon wafer. It was also observed that the precipitation of **5** from THF solution formed uniform rods with a diameter of 400 nm. The tunable nano- or microstructures of **5** from different solutions showed its potential applications in various integrated optoelectronic devices via solution process. The sharp X-ray diffraction peaks and the polarized optical microscopic images (POM) showed clearly that the 1D structures were highly ordered crystal (see the Supporting Information).[1c]

The single organic microwire transistor was fabricated utilizing the microwires precipitated from CH_2Cl_2 solution (1 mM). The wires with diameter of 500 nm to 1 μm were directly dropped on the *n*-octadecyltrichlorosilane (OTS)-treated SiO_2/Si substrate. The polyethylene (PE) fibers with 20 μm diameter as a shadow mask were mounted on the wafer, and a layer of 5 nm Cr followed by 100 nm gold was deposited onto the substrate by thermal evaporation under pressure of 4×10^{-4} Pa. Figure 3A illustrates the schematic of a typical FET from a single microwire.[1b,d–f] Figure 3B shows a representative microscope image of a Cr/Au top-contact device constructed from a single microwire of **5**. All the devices directly fabricated without annealing showed typical p-channel FET characteristics. More than 30 devices were tested with the hole mobility from 0.005 to 0.01 cm^2 V^{-1} s^{-1}, threshold from −18 to −31 V, and I_{on}/I_{off} about 10^3 under ambient conditions. Figure 3C and D illustrate transfer characteristics and transistor output of the microwire devices.

In summary, we have developed a facile approach to synthesize a novel π-extended condensed benzothiophene with rich sulfur atoms favoring $\pi-\pi$ interaction which could easily form bulk quantity individual microwires through self-assembly. The most convenient solution process was employed to fabricate the single microwire organic field-effect transistors. The organic transistors based on these microwires with the mobility of 0.01 cm^2 V^{-1} s^{-1} have been successfully achieved, which demonstrates that such process strategy for producing air-stable, good performance π-extended condensed benzothiophene is quite attractive. Further optimization of these transistors is underway.

Acknowledgment. This research was financially supported by the Major State Basic Research Development Program (Nos. 2006CB921602, 2007CB808000, and 2007CB936201) from the Ministry of Science and Technology, and by the National Natural Science Foundation of China (NSFC 50433030, 20521202, 20425207, and 20632020).

Supporting Information Available: Detailed experimental procedures and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kim, D. H.; Han, J. T.; Park, Y. D.; Jang, Y.; Cho, J. H.; Hwang, M.; Cho, K. *Adv. Mater.* **2006**, *18*, 719−723. (b) Tang, Q.; Li, H.; He, M.; Hu, W.; Liu, C.; Chen, K.; Wang, C.; Liu, Y.; Zhu, D. *Adv. Mater.* **2006**, *18*, 65−68. (c) Xiao, S.; Tang, J.; Beetz, T.; Guo, X.; Tremblay, N.; Siegrist, T.; Zhu, Y.; Steigerwald, M.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 10700−10701. (d) Tang, Q.; Li, H.; Liu, Y.; Hu, W. *J. Am. Chem. Soc.* **2006**, *128*, 14634−14639. (e) Tang, Q.; Li, H.; Song, Y.; Xu, W.; Hu, W.; Jiang, L.; Liu, Y.; Wang, X.; Zhu, D. *Adv. Mater.* **2006**, *18*, 3010−3014. (f) Sun, Y.; Tan, L.; Jiang, S.; Qian, H.; Wang, Z.; Yan, D.; Di, C.; Wang, Y.; Wu, W.; Yu, G.; Yan, S.; Wang, C.; Hu, W.; Liu, Y.; Zhu, D. *J. Am. Chem. Soc.* **2007**, *129*, 1882−1883.

(2) (a) Kastler, M.; Pisula, W.; Wasserfallen, D.; Pakula, T.; Müllen, K. *J. Am. Chem. Soc.* **2005**, *127*, 4286−4296. (b) Pisula, W.; Menon, A.; Stepputat, M.; Lieberwirth, I.; Kolb, U.; Tracz, A.; Stirringhaus, H.; Pakula, T.; Müllen, K. *Adv. Mater.* **2005**, *17*, 684−689.

(3) Huang, Y.; Duan, X.; Lieber, C. M. *Small* **2005**, *1*, 142−147.

(4) (a) Kim, D. H.; Lee, D. Y.; Lee, H. S.; Lee, W. H.; Kim, Y. H.; Han, J. I.; Cho, K. *Adv. Mater.* **2007**, *19*, 678−682. (b) Briseno, A. L.; Mannsfeld, S. C. B.; Lu, X.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Nano. Lett.* **2007**, *7*, 668−675.

(5) (a) Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606−608. (b) Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W.; Weber, W. *J. Appl. Phys.* **2002**, *92*, 5259−5263.

(6) (a) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604−12605. (b) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224−2225. (c) de Bettignies, R.; Nicolas, Y.; Blanchard, P.; Levillain, E.; Nunzi, J. M.; Roncali, J. *Adv. Mater.* **2003**, *17*, 1939−1943.

(7) (a) Wang, C.; Hu, R.; Liang, S.; Chen, J.; Yang, Z.; Pei, J. *Tetrahedron Lett.* **2005**, *46*, 8153−8157.

(8) (a) Pei, J.; Zhang, W.; Mao, J.; Zhou, X. *Tetrahedron Lett.* **2006**, *47*, 1551−1554. (b) Zhou, Y.; Liu, W.-J.; Zhang, W.; Cao, X.-Y.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Org. Chem.* **2006**, *71*, 6822−6828.

(9) (a) Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019−1027. (b) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 10587−10593. (c) Xiao, S.; Myers, M.; Miao, Q.; Sanaur, S.; Pang, K.; Steigerwald, M. L.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 7390−7394.

(10) Schwab, A. D.; Smith, D. E.; Rich, C. S.; Young, E. R.; Smith, W. F.; de Paula, J. C. *J. Phys. Chem. B* **2003**, *107*, 11339−11345.

(11) (a) Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 7390−7398. (b) Balakrishnan, K.; Datar, A.; Zhang, W.; Yang, X.; Naddo, T.; Huang, J.; Zuo, J.; Yen, M.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 6576−6577. (c) Balakrishnan, K.; Datar, A.; Oitker, R.; Chen, H.; Zuo, J.; Zang, L. *J. Am. Chem. Soc.* **2005**, *127*, 10496−10497.

JA075045F