ORGANIC
LETTERS

2007
Vol. 9, No. 21
4187−4190

Thin Film Organic Transistors from Air-Stable Heteroarenes: Anthra[1,2-*b*:4,3-*b*′:5,6-*b*′′:8,7-*b*′′′]tetrathiophene Derivatives

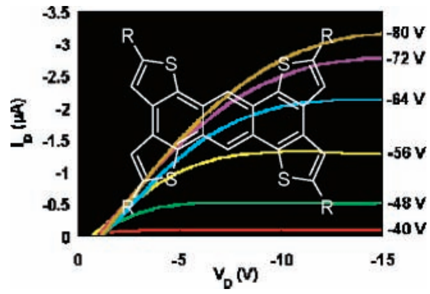
Wen-Jun Liu,[†] Yan Zhou,[†] Yuguo Ma,*[,†] Yong Cao,[‡] Jian Wang,*[,‡] and Jian Pei*[,†]

The Key Laboratory of Bioorganic Chemistry and Molecular Engineering and the Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Key Lab of Specially Functional Materials of Ministry of Education, Guangzhou 510640, China

jianpei@pku.edu.cn

Received July 17, 2007

ABSTRACT



A facile synthesis of air-stable anthra[1,2-*b*:4,3-*b*′:5,6-*b*′′:8,7-*b*′′′]tetrathiophene derivatives 1a and 1b has been developed for applications in organic thin film transistors. Both molecules tend to self-associate through π–π stacking in solution and in different films. The hole mobility of 0.012 cm^2 V^{-1} s^{-1} is obtained from 1a due to morphology changes in films from less ordered to highly ordered structures after thermal annealing. Good performance remained persistent over a period of 14 days, indicating the high stability of such transistors.

Organic field-effect transistors (OFETs) based on organic π-conjugated materials have attracted tremendous interest during the past decade in both academics and industry due to their potential applications in electronics.[1] The advantages of organic semiconductors, such as low cost, easy processing, compatibility with plastic substrates, and tunable properties offered by structure design, make them good alternatives to conventional inorganic materials.[1a,2]

Among all organic π-conjugated materials, pentacene and its derivatives have been considered as the most promising candidates for OFETs due to their high hole mobility.[3] The highest mobility of 1.5 cm^2 V^{-1} s^{-1} (on chemically modified SiO_2/Si substrate) from pentacene has been reported.[3a,b] However, the oxidative instability of pentacene, especially under applied electric fields, impedes its further applications in OFETs. Therefore, although significant achievements have been made in both the development of new organic materials

---

[†] Peking University.

[‡] South China University of Technology (SCUT).

(1) (a) Reese, C.; Roberts, M.; Ling, M.-M.; Bao, Z. *Mater. Today* **2004**, *7*, 20. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (c) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359.

(2) Forrest, S. R. *Nature* **2004**, *428*, 911.

(3) (a) Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606. (b) Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854. (c) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater.* **2003**, *15*, 1090.

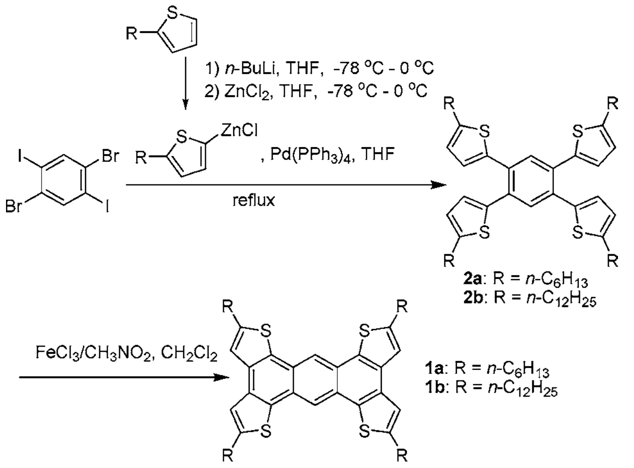
10.1021/ol701690y CCC: $37.00 © 2007 American Chemical Society
Published on Web 09/13/2007

and the optimization of techniques for device fabrication, developing new stable organic π-conjugated molecules with good charge carrier mobilities for thin film-based OFETs still offer intriguing challenges. Recent progress in searching for new organic materials for OFETs has demonstrated thiophene-based molecules as a novel class of organic semiconductors.[4] The electrical conductivities of oligothiophenes and thienylene-phenylene cooligomers have been systematically investigated.[4a−c] In order to avoid a sterically induced twist between proximal aromatics in said oligomers, fused thiophene aromatics were developed as new organic semiconductors.[4d−i] A variety of intra- and intermolecular interactions exhibited in these thiophene-based materials, such as van der Waals interactions, $\pi-\pi$ stacking, and sulfur−sulfur interactions, are essential to achieve high charge mobilities.[5]

Herein, we report the design and synthesis of two new organic semiconductors for OFETs, in which a fused heteroarene unit, anthra[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7-*b*‴]tetrathiophene, serves as the basic skeleton. Such π-extended planar core richly containing sulfur atoms is employed to facilitate molecular self-association driven by $\pi-\pi$ stacking. Theoretical calculations and experimental results suggest that the charge carrier is usually maximized along the direction of π-electron delocalization that is π-stacking orientation.[5,6] We have developed an expedient route to our target molecules **1a** and **1b** in two-step reaction sequences of Negishi cross-coupling followed by $FeCl_3$ oxidative cyclization. Both compounds exhibit good thermal and oxidative stability. The thin film transistors with carrier mobility of 0.01 cm^2 V^{-1} s^{-1} are easily realized from these molecules.

As illustrated in Scheme 1, the synthesis of **1a** and **1b** was commenced with the Negishi cross-coupling reaction between 1,4-dibromo-2,5-diiodobenzene and 5-alkyl-2-thienylzinc chloride, which was prepared in situ from the lithiation of 2-alkylthiophene with *n*-BuLi followed by the addition of anhydrous zinc chloride, furnishing **2a** and **2b** in 80% and 45% yields, respectively. Although other cross-coupling reactions including Kumada and Suzuki reactions were attempted, only the Negishi reaction produced **2a** and **2b** in ideal yields. The $FeCl_3$ oxidative cyclization protocol developed in our previous contributions was then utilized to construct the anthra[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7-*b*‴]tetrathiophene skeleton via thienyl−thienyl carbon−carbon bond formation.[7] As an effective way to construct polycyclic aromatic hydrocarbons, the oxidative cyclization reaction using ferric chloride was accomplished within 5 min under a mild condition to afford **1a** and **1b** in 68% and 65% yields, respectively. In our modular approach, the peripheral "R" group can be easily altered in a broad range, and thus, the intermolecular interaction and electronic characteristics of target molecules can be precisely tuned.

Scheme 1. Synthesis of Target Molecules **1a** and **1b**



Compounds **1a** and **1b**, isolated as pale yellow solids, are readily dissolved in common organic solvents, such as $CHCl_3$, CH_2Cl_2, THF, and toluene, which allowed us to purify them conveniently through flash column chromatography rather than vacuum sublimation usually used for the purification of insoluble organic semiconductors. ^{1}H and ^{13}C NMR spectra and MS associated with elemental analysis were employed to confirm the structure and purity of all compounds. The thermal decomposition temperature of 400 °C under nitrogen atmosphere revealed a good thermal stability of **1a** and **1b**. To elucidate the HOMO and LUMO energy levels of these molecules, and further understand their stabilities against oxygen, their electrochemical properties were investigated by cyclic voltammetry. The cyclic voltammetry of **1a** in thin films showed three irreversible oxidation peaks ($E_{1/2} = 1.28, 1.52, 1.78$ V) and an irreversible reduction peak ($E_{1/2} = -2.00$ V) vs Ag/AgCl.

The HOMO and LUMO energy levels in films were calculated from the onset of oxidation and reduction waves to be −5.57 and −2.64 eV, respectively. Thus, HOMO−LUMO band gap in films determined by their electrochemical properties was 2.93 eV, consistent to the value estimated from its absorption spectra in thin films. The HOMO level

---

(4) (a) Katz, H. E.; Laquindanum, J. G.; Lovinger, A. J. *Chem. Mater.* **1998**, *10*, 633. (b) Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G.; Ponomarenko, S.; Kirchmeyer, S.; Weber, W. *Adv. Mater.* **2003**, *15*, 917. (c) Mushrush, M.; Facchetti, A.; Lefenfeld, M.; Katz, H. E.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 9414. (d) Takimiya, K.; Kunugi, Y.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2005**, *127*, 3605. (e) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604. (f) Xiao, K.; Liu, Y.; Qi, T.; Zhang, W.; Wang, F.; Gao, J.; Qiu, W.; Ma, Y.; Cui, G.; Chen, S.; Zhan, X.; Yu, G.; Qin, J.; Hu, W.; Zhu, D. *J. Am. Chem. Soc.* **2005**, *127*, 13281. (g) Briseno, A. L.; Miao, Q.; Ling, M.-M.; Reese, C.; Meng, H.; Bao, Z.; Wudl, F. *J. Am. Chem. Soc.* **2006**, *128*, 15576. (h) 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.* **2006**, *129*, 1882. (i) Valiyev, F.; Hu, W.-S.; Chen, H.-Y.; Kuo, M.-Y.; Chao, I.; Tao, Y.-T. *Chem. Mater.* **2007**, *19*, 3018.

(5) (a) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926. (b) Lemaur, V.; da Silva Filho, D. A.; Coropceanu, V.; Lehmann, M.; Geerts, Y.; Piris, J.; Debije, M. G.; van de Craats, A. M.; Senthilkumar, K.; Siebbeles, L. D. A.; Warman, J. M.; Brédas, J.-L.; Cornil, J. *J. Am. Chem. Soc.* **2004**, *126*, 3271.

(6) Che, Y.; Datar, A.; Yang, X.; Naddo, T.; Zhao, J.; Zang, L. *J. Am. Chem. Soc.* **2007**, *129*, 6354.

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

of **1a** (−5.57 eV) was lower than that of pentacene (−4.60 eV),[3c] and thus, it was more stable than pentacene against oxygen.

It was observed that two singlet signals in ^{1}H NMR spectra of **1a** and **1b** assigned to the protons in *meso*-benzene and thiophene rings, respectively, shifted upfield by approximately $\Delta\delta = 0.1$ ppm (for example, the proton of **1b** in *meso*-benzene ring moved from 8.69 to 8.59 ppm, and another proton in thiophene rings moved from 7.36 to 7.30 ppm) as the solution was concentrated from 4 to 20 mg/mL in $CDCl_3$. Such an upfield shift was attributed to the intermolecular shielding from the neighboring aromatic molecules in concentrated solution, implying their tendency to self-associate through $\pi-\pi$ stacking between molecules.[8]

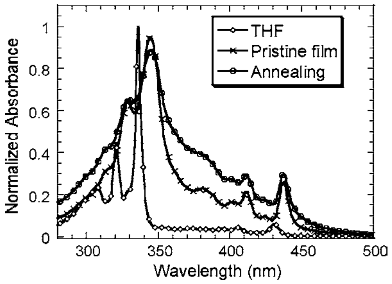


Figure 1. Absorption spectra of **1a** in dilute solution (10^{-6} M) and both in pristine film and in annealing film.

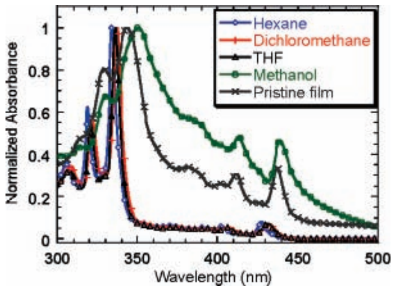


Figure 2. Absorption spectra of **1b** in different solvents (10^{-5} M) and in thin film.

Figure 1 illustrates absorption and emission spectra of **1a** in dilute solution and in thin film. Both **1a** and **1b** exhibited similar photophysical properties due to their identical skeletons, the anthra[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7-*b*‴]tetrathiophene unit. The absorption of **1a** in dilute THF solution (10^{-6} M) showed the absorption maximum at 336 nm with a small peak at 431 nm. Compared with that in solution, the absorption spectrum of **1a** in spin-cast film became less structured. The maximum absorption red-shifted about 9 nm from 336 to 345 nm, while the small peak at 431 nm red-shifted about 6 nm to 437 nm accompanied with obvious absorbance enhancement. After annealing at 180 °C for 1 h, the absorption spectrum further broadened and the absorption maximum was slightly red-shifted. Their absorption behaviors in different solvents were also investigated. Figure 2 shows the absorption spectra of **1b** in different solvents and in thin film as an example. The absorption spectra of **1a** and **1b** were similar in *n*-hexane, dichloromethane, and THF. However, significant broadening of the absorption spectrum and red-shift of all the peaks with a concomitant absorbance enhancement around 430 nm, in dilute methanol solution, were observed, which was similar to that in the pristine film by spin-casting due to the formation of the aggregates. Such pronounced change of the absorption spectrum is a result of the delocalization of the exciton within a co-facial stack induced by the $\pi-\pi$ interaction, which was also evidenced by a related red-shift of photoluminescence spectrum shown in Figure 3.[9] The emission of **1a** in dilute solution showed the maximum at 437 nm with a shoulder at 460 nm, whereas the emission spectrum of **1a** in thin films exhibited a maximum at 469 nm with a second feature at 508 nm. More interestingly, one of the emission peaks at 469 nm shown in pristine film disappeared after thermal annealing at 180 °C for 1 h, suggesting the formation of highly ordered structures in the film.

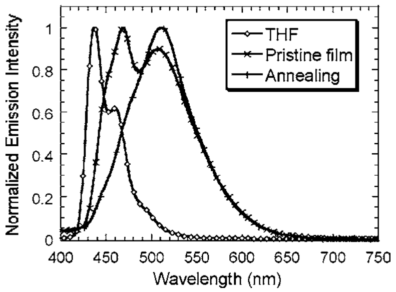


Figure 3. Emission spectra of **1a** in dilute solution (10^{-6} M) and both in pristine film and in annealing film. Emission spectra were obtained upon excitation at the absorption maximum.

Organic field-effect transistors (OFETs) were fabricated in a “top contact” configuration as follows: a thin film of semiconductor **1a** with the thickness of 50 nm was vacuum-evaporated onto an OTS-treated SiO_2 (300 nm)/Si substrate as an active layer, and gold was then vacuum-deposited as the source/drain electrode. Compound **1a** performed as a *p*-channel transistor. Before annealing, the transistors exhibited low mobility, on the order of 10^{-4} cm^2 V^{-1} S^{-1}, with an on/off ratio of 5×10^3. However, after annealing the thin film at 230 °C for 20 min, the device performance was significantly improved. Figure 4 shows output and transfer characteristics of OFET devices after thermal annealing. The calculated hole mobility was 0.012 cm^2 V^{-1} S^{-1} from the

---

[8] (a) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 10587. (b) Xiao, S.; Myers, M.; Miao, Q.; Sanaur, S.; Pang, K.; Steigerwald, M. L.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 7390.

[9] 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.

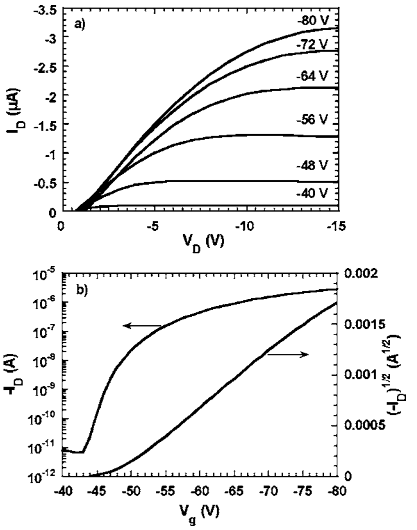


Figure 4. Electrical characterization of OFETs after thermal annealing: (a) plots of I_D vs V_D at various gate voltages; (b) plots of I_D and $I_D^{1/2}$ vs V_g at constant $V_D = -60$ V.

transfer curve, 2 orders of magnitude larger than that before annealing. The on/off ratio was as high as 10^5. Reproducible results were obtained from different transistors. We attributed this remarkable improvement to the morphology change of the active layer by heating, which was confirmed by the difference between the absorption and emission spectra of **1a** in thin films before and after thermal annealing as described above. The morphology of the films on OTS-treated SiO_2 (300 nm)/Si substrate was also directly imaged with tapping mode AFM. As shown in Figure 5, the newly prepared unheated film consisted of microcrystalline grains with the size of about 0.01 μm^2 and a height around 15 nm. However, after thermal annealing, the film reorganized into large crystalline terraces up to 25 μm^2. The height was about 50 nm. The increased grain size and decreased grain boundaries in the films after thermal annealing contributed to the increased hole mobility and on/off ratio.[4i] The almost identical transistor performance acquired after 14 days indicated the stability of the semiconductor under ambient conditions.

In summary, we have synthesized two sulfur-rich anthra-[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7-*b*‴]tetrathiophene-based heteroarenes favoring $\pi-\pi$ interaction in a facile manner. The characterization by ^{1}H NMR and the investigation of photophysical properties of these two molecules in solution and in different films indicate that such molecules tend to self-associate through $\pi-\pi$ stacking. The hole mobility of 0.012 cm^2 V^{-1} s^{-1} is obtained from **1a** after thermal annealing. Such notable enhancement of hole mobility demonstrates the heat driven morphology change in films from less ordered to highly ordered structures. The good performance remained persistent over a period of 14 days, indicating the high stability of such transistors. Our results shed light on developing strategy for air-stable, good-performance organic semiconductors. Further optimization of these transistors is underway.

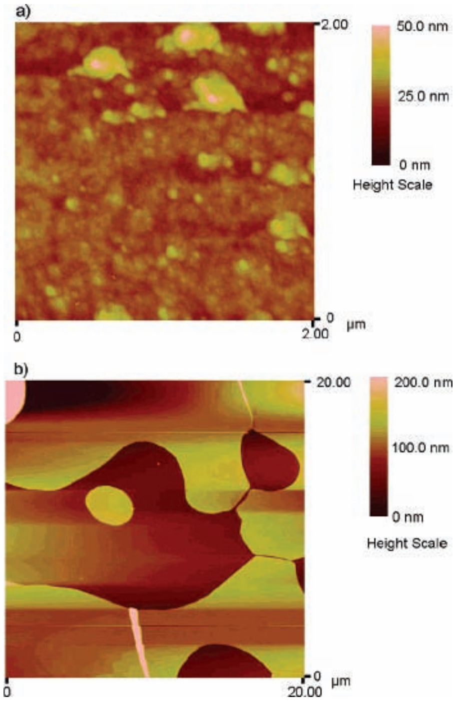


Figure 5. AFM images of thin films of **1a**: (a) pristine; (b) after heating to 230 °C for 20 min.

Acknowledgment. This research was financially supported by the Major State Basic Research Development Program (Nos. 2006CB921602 and 2007CB808000) from the Ministry of Science and Technology and by the National Natural Science Foundation of China (NSFC 50433030, 20521202, 20425207, 20632020). We are grateful to Prof. Junbiao Peng, Mr. Linfeng Lan, and Mr. Lei Wang at SCUT for experimental help and useful discussions.

Supporting Information Available: Experimental procedures and ^{1}H and ^{13}C NMR data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL701690Y