4188 *Chem. Mater.* **2008,** *20,* 4188–4190

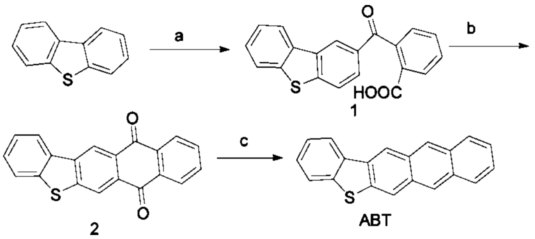
Anthra[2,3-*b*]benzo[*d*]thiophene: An Air-Stable Asymmetric Organic Semiconductor with High Mobility at Room Temperature

Chunyan Du,[†,‡] Yunlong Guo,[†,‡] Yunqi Liu,*[,†]
Wenfeng Qiu,[†] Hengjun Zhang,[†,‡] Xike Gao,[†,‡]
Ying Liu,[†,‡] Ting Qi,[†,‡] Kun Lu,[†,‡] and Gui Yu[†]

Beijing National Laboratory for Molecular Science, Key Laboratory of Organic Solids, Institute of Chemistry, and Graduate School, Chinese Academy of Sciences, Beijing 100190, China

Received May 14, 2008

Scheme 1. Synthesis of ABT[a]



[a] Reagents and conditions: (a) Phthalic anhydride, AlCl$_3$, r.t., 4 h; (b) AlCl$_3$, PCl$_5$, reflux, 12 h; (c) LiAlH$_4$, THF, 3 h.

Organic field-effect transistors (OFETs) have attracted much attention in the context of large-area, flexible, and ultralow-cost electronics, such as radio frequency identification tags, smart cards, and organic active matrix displays.[1] As the core element of an OFET, organic semiconductors with high performance and excellent stability are necessary for commercial applications. Recently, many novel organic semiconductors with higher mobilities than that of amorphous silicon (0.1 cm^2 V^{-1} s^{-1}) have been developed.[1,2] Among these, pentacene with the highest reported FET mobility (a value above 1.5 cm^2 V^{-1} s^{-1})[3] became the benchmark for FET devices. The extended π systems of linearly condensed [*n*]acenes enhance the intermolecular overlap of $\pi-\pi$ systems in the solid state and lead to high mobility.[4] However, pentacene suffers from the disadvantages of oxidative instability, extreme insolubility, and for display applications, a strong absorbance throughout the visible spectrum.[5] Many groups are working on developing practical OFET materials that ensure not only high performance but also high stability in the operational environment. Notably, heteroarenes such as thieno[*n*]acenes[6] and thiophene−benzene fused compounds,[7,8] with a minor change of the long, platelike molecular shape of pentacene, have been intensely studied. The heteroatom effects not only on the electronic structures but also on the solid-state structures[9] made thiophene-fused aromatics attractive candidates. Our group has fabricated pentathienoacene (PTA) as active semiconducting layers for OFETs previously,[6] PTA combining the stability of the thiophene ring with the planarity of linear acenes shows good stability and further indicates that thiophene based materials are a promising class of organic materials for their use in OFETs.

However, most of these compounds are linear, center-symmetric molecules. Until now, there are only a few asymmetric organic semiconductors used as the active semiconducting layers in OFETs,[8b,10] due to the lack of efficient synthetic strategies. In most cases, the asymmetric heteroarenes were proved to have comparable or even better performance in contrast to their symmetric counterparts.[10b] For example, tetraceno[2,3-*b*]thiophene, having a fused thiophene unit at one side asymmetrically, has a high mobility of up to 0.47 cm^2 V^{-1} s^{-1},[8b] which is higher than that of most similar symmetric heteroacene compounds.[8c,d] Besides, some unique characteristics can be found in asymmetric compounds and investigation of asymmetric organic semiconductors would be helpful in understanding the mechanism of growth of organic thin films by molecular vapor deposition.[10b] As a result, the exploration of asymmetric organic semiconductors would be promising.

Anthra[2,3-*b*]benzo[*d*]thiophene (ABT, Scheme 1) as an asymmetric pentacene analogy has been synthesized previously in five steps,[11] but its solid-state structure and semiconducting characteristics have not been developed. On the basis of the ring system, ABT would be expected to have a higher oxidation barrier because of the greater loss of aromaticity than pentacene.[8d] Also, with the introduction of the sulfur atom, ABT is expected to interact efficiently through intermolecular S$\cdots$S or S$\cdots\pi$ contacts which can provide an alternative charge transport pathway other than

---

* To whom correspondence should be addressed. E-mail: liuyq@ mail.iccas.ac.cn.

[†] Institute of Chemistry.

[‡] Graduate School.

(1) (a) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (b) Sun, Y.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2005**, *15*, 53. (c) Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (d) Di, C.-a.; Yu, G.; Liu, Y.; Zhu, D. *J. Phys. Chem. B* **2007**, *111*, 14083.

(2) Takimiya, K.; Kunugi, Y.; Otsubo, T. *Chem. Lett.* **2007**, *36*, 578.

(3) (a) Lin, Y.; Gundlach, D.; Nelson, S.; Jackson, T. *IEEE Trans. Electron. Devices* **1997**, *44*, 1325. (b) Kelley, T.; Muyres, D.; Baude, P.; Smith, T.; Jones, T. *Mater. Res. Symp. Proc.* **2003**, *771*, L6.5.1.

(4) Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1159–1162.

(5) Yamada, M.; Ikemoto, I.; Kuroda, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1057–1062.

(6) 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.

(7) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.

(8) (a) Gao, J.; Li, R.; Li, L.; Meng, Q.; Jiang, H.; Li, H.; Hu, W. *Adv. Mater.* **2007**, *19*, 3008. (b) Tang, M. L.; Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2006**, *128*, 16002. (c) Ebata, H.; Miyazaki, E.; Yamamoto, T.; Takimiya, K. *Org. Lett.* **2007**, *9*, 4499. (d) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664.

(9) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Am. Chem. Soc.* **2002**, *124*, 10638.

(10) (a) Valiyev, F.; Hu, W.-S.; Chen, H.-Y.; Kuo, M.-Y.; Chao, I.; Tao, Y.-T. *Chem. Mater.* **2007**, *19*, 3018. (b) Tang, M. L.; Roberts, M. E.; Locklin, J. J.; Ling, M. M.; Meng, H.; Bao, Z. *Chem. Mater.* **2006**, *18*, 6250. (c) Deman, A. L.; Tardy, J.; Nicolas, Y.; Blanchard, P.; Roncali, J. *Synth. Met.* **2004**, *146*, 365.

(11) (a) Tedjamulia, M. L.; Tominaga, Y.; Castle, R. N. *J. Heterocyclic Chem.* **1983**, *20*, 861. (b) Mayer, F. *Ann. Chem.* *488*, 259.

10.1021/cm801305f CCC: $40.75

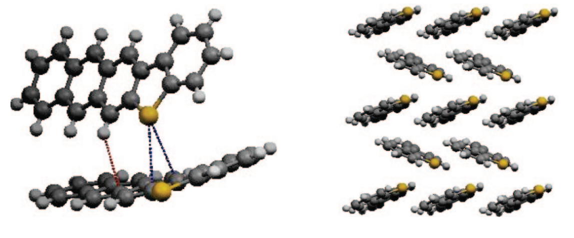


Figure 1. (a) Molecule structure of ABT. C···S contacts (blue dots, 3.34 Å) and CH···π contacts (red dots, 2.88 Å). (b) Stacking structure of ABT with a view down the *b* axis. Sulfur atoms are yellow, carbon atoms are gray, and hydrogen atoms are white.

π−π interactions.[12] All these merits suggest that ABT is a promising candidate for FETs. In this communication, we present a facile synthesis of ABT in only three steps; the single crystal structure of ABT and electrical property were studied. Compared with pentacene, ABT has a larger band gap and is therefore expected to be stable in air. OFETs based on ABT have been constructed and a mobility up to 0.41 $cm^2 V^{-1} s^{-1}$ has been achieved with devices deposited onto octadecyltrichlorosilane (OTS)-treated SiO_2/Si substrates held at room temperature. To the best of our knowledge, this mobility is comparable to the highest mobility values reported for core-asymmetric organic semiconductors.[8b] More importantly, the devices exhibits good air stability for more than three months.

The compound ABT was prepared according to Scheme 1 in three steps, starting from commercially available dibenzothiophene. Friedel−Crafts reaction of dibenzothiophene and phthalic anhydride gave **1** in 85% yield.[11a] **1** was treated with aluminum chloride anhydrous and phosphorus pentachloride to afford **2** in 70% yield. The final product ABT was achieved through a facile reduction of **2** with $LiAlH_4$[10a] as yellow powder. Unlike pentacene, ABT is moderately soluble in common solvents such as THF, toluene, and chlorobenzene; thus, it could be easily purified by recrystallizations. The structure of ABT was determined by electron ionization MS, high resolution MS, ^1H NMR, elemental analyses, and X-ray crystallography.

Crystals of ABT suitable for single-crystal X-ray diffraction (XRD) studies were grown from toluene and hexane solutions. As shown in Figure 1, the crystal structure contains an almost planar ABT molecule stacked along the *b*-axis direction assuming a herringbone geometry similar to that of pentacene.[13] Remarkably, marked S···C short contacts (3.34 Å) shorter than the nonbonded S···C contact distance observed in most organic crystal structures (3.61 Å)[14] were found between the neighboring molecules, which led to a more densely stack of ABT than pentacene.[13] The short CH···π and C···S contacts existing in a face-to-edge manner suggest a two-dimensional electronic structure of the crystal. The double channel fashion is envisioned to be transformed into the facile establishment of a high-performance charge transport system.

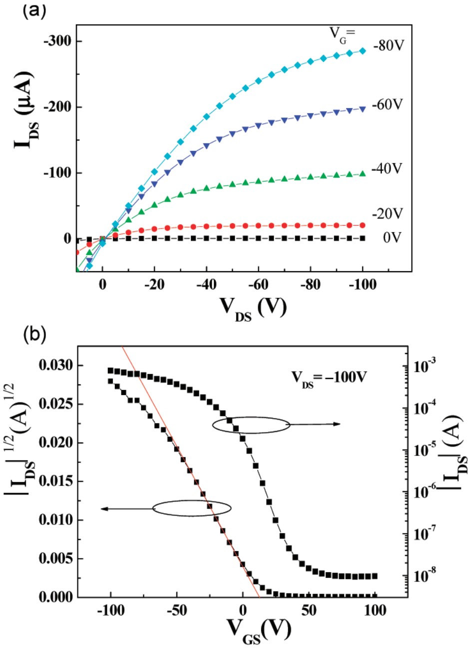


Figure 2. (a) Output characteristics and (b) transfer characteristics of a device of ABT deposited on the OTS/SiO_2/Si substrate at 20 °C (channel length 50 μm, channel width 3 mm).

The physical properties of ABT were characterized by thermogravimetric analysis (TGA), UV−vis spectroscopy, and cyclic voltammetry (CV). No decomposition was observed for ABT until about 300 °C, suggesting a good thermal stability of the compound. The UV−vis spectrum of the vacuum-deposited ABT thin film revealed an absorption maximum at 468 nm, and it was about 33 nm red-shifted compared with that in CH_2Cl_2 solution (435 nm), suggesting there were strong intermolecular interactions in the thin film. The optical band gaps of ABT, determined by extrapolating the long-wavelength absorption edge of the thin film, is 2.5 eV, and is higher than that of pentacene (2.06 eV).[15] The CV of ABT in CH_2Cl_2 showed a reversible oxidation peak, and the oxidation potential is about 1.15 V vs Ag/AgCl. The relatively high oxidation potential of ABT compared to that of pentacene (0.64 eV)[15] resulted in better oxidation stability of the compound. The HOMO level of ABT, estimated from the onset oxidation potential relative to vacuum was −5.35 eV, about 0.75 eV lower than that of pentacene (−4.60 eV).[15] It is worth noting that the HOMO level of ABT matches well with the work function of gold metal (5.2 eV)[16] so that the hole injection from the gold source electrode in OFETs is expected to be efficient.

OFET devices were fabricated in a top-contact configuration with thin films of ABT deposited onto SiO_2/Si, OTS treated SiO_2/Si as active organic semiconductor layers. All the devices showed typical p-channel transistor characteristics under ambient conditions (see Supporting Information). The typical output and transfer characteristics of ABT are shown in Figure 2. The main parameters of device performance, that is, mobility (μ_{FET}), threshold voltage (V_T), and I_{on}/I_{off} at different substrate temperatures (T_{sub}), are summarized in

---

(12) Briseno, A. L.; Miao, Q.; Ling, M.-M.; Reese, C.; Meng, H.; Bao, Z.; Wudl, F. *J. Am. Chem. Soc.* **2006**, *128*, 15576.

(13) Bromley, S. T.; Mas-Torrent, M.; Hadley, P.; Rovira, C. *J. Am. Chem. Soc.* **2004**, *126*, 6544.

(14) (a) Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 7384. (b) Gao, X.; Dou, J.; Li, D.; Dong, F.; Wang, D. *J. Chem. Crystallogr.* **2005**, *35*, 107.

(15) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C. H. *Adv. Mater.* **2003**, *15*, 1090.

(16) Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B.-C.; Van Patten, P. G.; Bao, Z. *Chem. Mater.* **2003**, *15*, 1778.

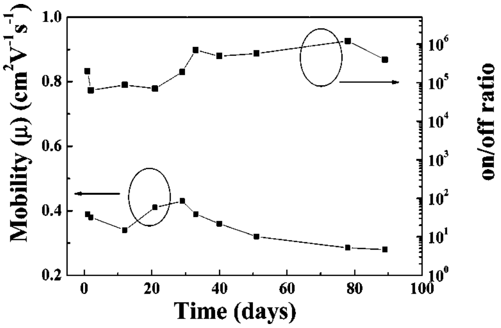


Figure 3. Field effect mobility and on/off ratio for ABT devices tested over a period of three months.

Table S1, Supporting Information. The μ_{FET} decreases with the increase of the substrate temperature, mostly due to the formation of grain aggregations of the thin films at higher substrate temperature, which can be confirmed by XRD and atomic force microscopy (AFM) as shown below. The best performance with a mobility of 0.41 cm^2 V^{-1} s^{-1} and I_{on}/I_{off} of about 10^5 was obtained when ABT was deposited on OTS/SiO$_2$/Si at T_{sub} = 20 °C. As compared with other pentacene analogues that showed good performance at high substrate temperature, ABT exhibits a great advantage for low-cost device fabrication without increasing the substrate temperature and use of flexible plastic substrates which cannot withstand high temperatures.[8a] To test the device stability, OFET devices were stored in air, and the actual testing was also performed under ambient conditions. As shown in Figure 3, in a period of three months, the mobility values ranged from 0.28−0.45 cm^2 V^{-1} s^{-1} with the corresponding on/off ratios varying slightly from 10^5 to 10^6. The fluctuation in mobility and on/off ratio may be due to the humidity fluctuations as the storage and test were all performed under ambient conditions, which have been observed for many other organic semiconductors.[17] All the results demonstrate that ABT with both high mobility and good air stability is a promising semiconducting material for application in OFETs.

The orientation of the thin film was investigated by means of XRD analysis. Figure 4 shows XRD patterns of thin films of ABT deposited on OTS treated SiO$_2$/Si at different T_{sub} values. We observed peaks up to the forth order for ABT at T_{sub} = 20 °C, indicating a high degree of order and crystallinity. The higher order peaks became weaker until they disappeared with increasing substrate temperature, which corresponds well with correlation between the mobility and the substrate temperature. The *d*-spacing calculated from the first diffraction peak at 2θ of 6.14° is 14.4 Å, compared with the molecular length of ABT (13.5 Å) determined by single crystal XRD experiments, suggesting the ABT molecule was standing near upright on OTS/SiO$_2$/Si surface and formed a perfectly packed structure. Such orientation is known to be favorable for achieving high mobility since the stacking structure would increase the intermolecular π overlap[18] and the stacking direction is also consistent with the direction of current flow.[10a]

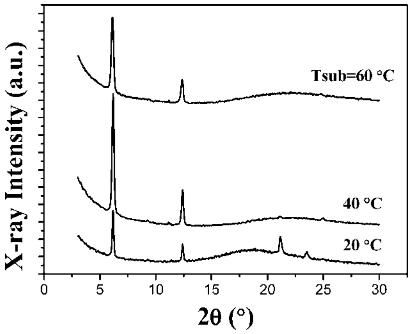


Figure 4. X-ray diffraction of 50 nm thick film of ABT deposited on OTS/SiO$_2$/Si surface at different substrate temperatures.

To better understand the relationship between the film morphology and the mobility, the thin films of ABT on different substrate surfaces were investigated by AFM (see Supporting Information). The film on OTS/SiO$_2$/Si consists of an almost continuous molecular layer with less grain boundaries than the film on untreated SiO$_2$/Si, which may account for higher performance of the former. As the substrate temperature was increased, the grains became larger, however, with the formation of some aggregations, which may be related to the drop in mobility. Further investigations of the dependence of the mobility on substrate temperature are under way. Structure−property relationships among asymmetric and symmetric organic semiconductors will be described in detail elsewhere.

In conclusion, an asymmetric heteroacene compound ABT has been facilely synthesized, and its solid-state structure and thin film characteristics were also characterized. FETs fabricated with ABT showed a mobility as high as 0.41 cm^2 V^{-1} s^{-1} at room temperature, which facilitates the use of any type of plastic substrates. Most importantly, these devices showed good air stability under ambient conditions even for more than three months. Our results suggested that exploration of asymmetric organic semiconductors would be extremely promising for the application in organic electronics.

Acknowledgment. The present research was financially supported by National Natural Science Foundation (20573115, 60736004, 20721061, 60671047, 50673093), the Major State Basic Research Development Program (2006CB806200, 2006CB932100), and the Chinese Academy of Sciences.

Supporting Information Available: The synthesis, EI, HRMS, crystallographic information file (CIF), TGA, UV/vis absorption spectra and CV of ABT, the fabrication and characterization of OFET based on the films of ABT, and AFM of the thin films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM801305F

---

(17) Li, D.; Borkent, E.-J.; Nortrup, R.; Moon, H.; Katz, H.; Bao, Z. *Appl. Phys. Lett.* **2005**, *86*, 42105.

(18) DeLongchamp, D. M.; Sambasivan, S.; Fischer, D. A.; Lin, E. K.; Chang, P.; Murphy, A. R.; Fréchet, J. M. J.; Subramanian, V. *Adv. Mater.* **2005**, *17*, 2340.