

# Benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene as solution processible organic semiconductor for field-effect transistors†

Peng Gao, Dirk Beckmann, Hoi Nok Tsao, Xinliang Feng, Volker Enkelmann, Wojciech Pisula‡ and Klaus Müllen\*

Received (in Cambridge, UK) 14th November 2007, Accepted 4th January 2008

First published as an Advance Article on the web 25th January 2008

DOI: 10.1039/b717608b

**Coplanar benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophenes (1a, 1b) for the application in organic field-effect transistors were synthesized by a simple two-step procedure involving triflic acid induced ring-closure reaction; such solution processed devices show a hole mobility of up to 0.01 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.**

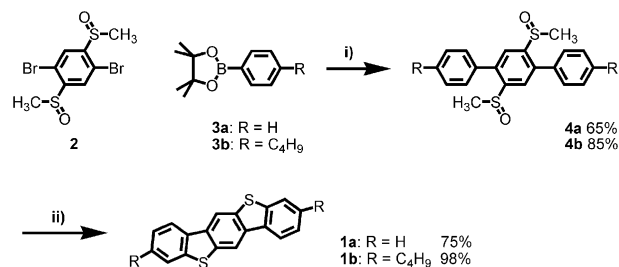
Conjugated oligomers with rigid, fused-ring structures are of particular interest for organic field-effect transistors (OFETs). Among all the organic  $\pi$ -conjugated materials, pentacene and their derivatives have been considered as the benchmark materials for OFETs due to their high charge carrier mobility comparable to amorphous silicon.<sup>1</sup> However, their stability is somehow limited.<sup>2</sup> Recent developments by several groups in synthesizing new organic semiconductors and optimizing device fabrication have resulted in improved stability and transistor performance.<sup>3</sup> Some of these materials were based on fused thiophene (selenophene) aromatics and indeed led to good OFET characteristics (mobility up to 0.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and on/off ratio up to 10<sup>6</sup>),<sup>4</sup> together with higher stability than that of pentacene.

Motivated by this, benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene (BBBT, **1a**), which is an analogue of pentacene, with a similar rigid, linearly conjugated structure,<sup>5</sup> was synthesized and applied in OFETs. Very recently, OFET properties of physical vapor deposited BBBT films have been investigated, resulting in a hole mobility of  $2.4 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> but faced the problem of a complicated synthesis.<sup>6</sup> In our parallel studies, we herein report a new simple, straightforward, and high yield synthesis of BBBT and its alkyl substituted derivative, which were then applied in OFETs *via* solution processing, giving a hole mobility of up to 0.01 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off ratio of 10<sup>5</sup>.

Scheme 1 illustrates the synthetic approach towards BBBT **1a** and **1b**. Precursor **2** was easily obtained by following the procedure described in the literature.<sup>7</sup> The Suzuki coupling between **2** and the corresponding phenyl boronic ester afforded **4a** and **4b** in 65 and 85% yields, respectively. The

quantitative intramolecular ring-closing condensation<sup>8</sup> of the dimethylsulfinyl benzene with the adjacent phenyl ring proceeded slowly in the dark with an excess of pure triflic acid. After 72 h, the clear solution was poured into a water/ice mixture to give a yellowish powder which was filtered off, dried and used directly in the next step without further purification. The powder was dissolved in pyridine and heated to reflux overnight. The product was purified by recrystallization from tetrachloroethane or by silica chromatography, giving pure BBBT **1a** and BBBT-C4 **1b** as colorless solids in 75 and 98% yields, respectively.<sup>9</sup> The alkyl substituents in **1b** dramatically increase the solubility of this material, which can be easily dissolved in common organic solvents at room temperature. To the best of our knowledge, no synthetic method has been reported for endcapping of BBBT by alkyl chains. In our modular approach, the peripheral “R” group can be simply altered in a broad range, such as alkyl or aryl, and thus, the intermolecular interactions and electronic characteristics of the target molecules can be precisely tuned.

The optical properties and redox potentials of compounds **1a** and **1b** are shown in Fig. 1 and Table 1. The absorption maxima of the ring-fused derivatives **1a** and **1b** are obviously red-shifted with respect to those of the precursors (Fig. 1). Both **1a** and **1b** possess similar absorption bands, indicating no pronounced perturbation by the substitution of alkyl chains, although the main absorption band of **1a** was slightly blue-shifted (366 nm for **1a** and 369 nm for **1b**). Oxidation potentials of **1a** and **1b** were investigated by cyclic voltammetry (CV). Both **1a** and **1b** exhibited similar and reversible oxidation waves. Their HOMO levels around -5.4 eV are lower than that observed for pentacene and most oligothiophenes, indicating better environmental stability. Taking the HOMO-LUMO gap of around 3.3 eV, as estimated from the

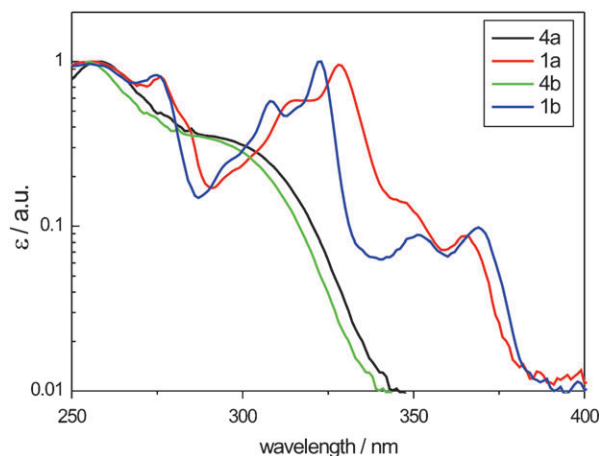


**Scheme 1** Synthetic route towards BBBT **1a** and **1b**. Reagents and conditions: (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene, 80 °C, 24 h; (ii) (a) CF<sub>3</sub>SO<sub>3</sub>H, P<sub>2</sub>O<sub>5</sub>, RT; (b) pyridine, reflux.

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany. E-mail: muellen@mpip-mainz.mpg.de; Fax: +49 6131 379100; Tel: +49 6131 3790

† Electronic supplementary information (ESI) available: Synthesis of oligomers, single-crystal structure, FET device fabrication, X-ray diffraction and PL spectra. See DOI: 10.1039/b717608b

‡ Present address: Evonik Degussa GmbH, Process Technology & Engineering, Process Technology—New Processes, Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang, Germany.

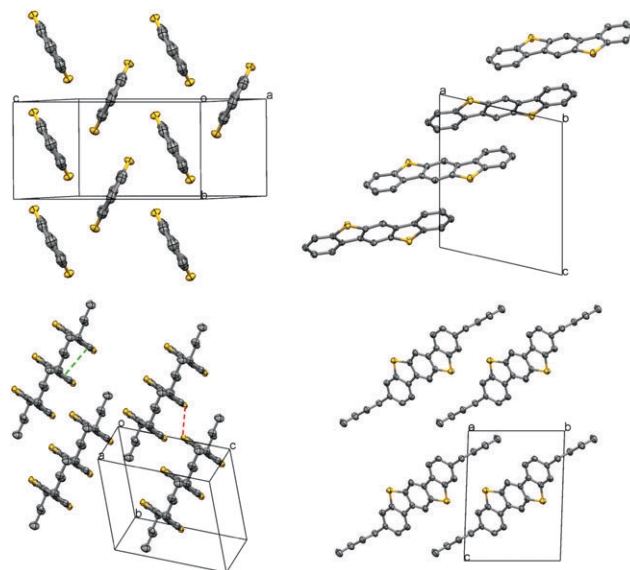


**Fig. 1** UV-Vis spectra of **1** and **4** in THF ( $1.0 \times 10^{-6}$  M).

absorption edges in THF, the LUMO levels of  $-2.1$  eV can be calculated.

Single crystals of **1a** and **1b** suitable for X-ray analysis were obtained by recrystallization from tetrachloroethane and chloroform, respectively (Fig. 2). In both structures, the molecules are located on an inversion centre and the entire  $\pi$ -systems are planar. The mean atom deviations from the plane based on the  $C_{18}S_2$  skeleton are  $0.03$  Å for both **1a** and **1b** (Fig. S1, ESI†). Interestingly, the packing regime of **1a** shows no prominent  $\pi$ -stacking in comparison to the literature<sup>6</sup> but instead a typical “herringbone” structure like pentacene, in which there is no molecular overlap (Fig. 2(a)). The molecular structure of **1b** is similar to **1a** except for the two terminal *n*-butyl groups, which lie out of the plane of the skeleton and adopt a staggered and all-*anti* conformation to minimize the steric energy in the packing of aliphatic chains. Therefore the stretched and doubly bent **1b** promotes a “lamellar” structure<sup>10</sup> with an interplanar separation of  $3.42$  Å as marked in green dashed lines (Fig. 2(b)). A side-by-side S–S short distance of  $3.80$  Å is determined which is indicated by red dashed lines in Fig. 2(b).

Organic field-effect transistors (OFETs) are fabricated in a “bottom contact” configuration as follows: compound **1a** is drop-cast from a  $5 \text{ mg ml}^{-1}$  1,1,2,2-tetrachloroethane solution on photolithographically defined transistor substrates, where the dielectric surface is treated with phenyltriethoxysilane (PTES) in order to avoid interfacial trapping. Fig. 3(a) illustrates the transfer characteristics after annealing the sample at  $100$  °C for 30 min. From these curves, a saturated hole mobility of  $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is obtained, which is applied to the real channel length in consideration of the spotlike film formation (ESI†). Furthermore a threshold voltage  $V_T$  of



**Fig. 2** Crystal structures of **1a** (a) and **1b** (b), in which the H atoms are omitted for clarity. (Green dashed line marks interplanar separation of  $3.42$  Å; red dashed line indicates S–S short distance of  $3.80$  Å).

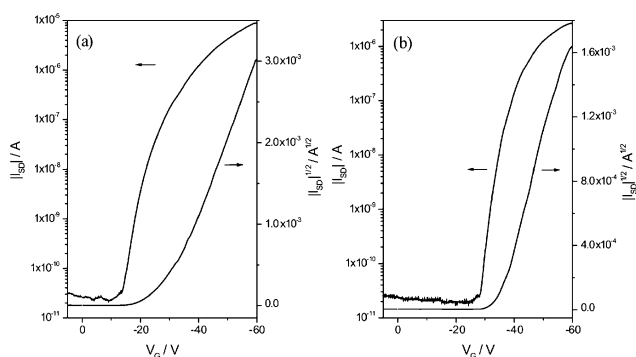
$-29$  V and an on/off current ratio of  $10^5$  are extracted (Table 2). It is interesting to compare this higher charge carrier mobility with the value reported for vacuum deposited BBBT of  $2.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>6</sup> However, the high threshold voltage together with the superlinear increase of the source–drain current in the output curves (ESI†) suggests interface trapping and high contact resistances. We attribute these limiting factors to the rigidity of the crystals lying between the electrodes, in this way preventing sufficient contact to the interface and the metals. It is believed that the device fabrication can be further improved, most probably leading to significantly enhanced overall performance.

Due to its low solubility, compound **1a** is difficult to process. To improve the solubility and thus the processibility, dibutylated BBBT (**1b**) is therefore synthesized, allowing film deposition from most common organic solvents like THF, chloroform or toluene. Using the same processing conditions as **1a**, **1b** resulted in a lower mobility of  $1 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , a threshold voltage of  $-27$  V and an on/off ratio of  $10^2$ . The best result for this compound is achieved by drop-casting a  $20 \text{ mg ml}^{-1}$  toluene solution on a transistor substrate held at  $60$  °C. The bottom contact gold electrodes are treated with 1-octanethiol to reduce contact resistance.<sup>11</sup> Despite the high crystallinity and large domains (ESI†), compound **1b** reveals an one order of magnitude lower charge carrier mobility than **1a** (Table 2), possibly due to the isolating property of the alkyl chains which leads to a hindered charge transport inside the

**Table 1** Electrochemical results, UV-Vis data and estimated HOMO and LUMO levels of **1a** and **1b**

Compound	$E_{\text{ox}}^a/\text{V}$ Anodic/onset	$\lambda_{\text{max}}^b/\text{nm}$ Peak/edge	HOMO <sup>c</sup> /eV	Band gap <sup>d</sup> /eV	LUMO/eV
<b>1a</b>	1.07/0.95	366/379	$-5.4$	3.30	$-2.1$
<b>1b</b>	1.07/0.96	369/375	$-5.4$	3.24	$-2.2$

<sup>a</sup> Vs. Ag/AgCl in  $\text{CH}_2\text{Cl}_2$  with  $0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6$  as supporting electrolyte (scan speed =  $50 \text{ mV s}^{-1}$ ). <sup>b</sup> Absorption spectra. <sup>c</sup> Calculated based on HOMO =  $-(E_{\text{ox}}^{\text{onset}} + 4.4) \text{ eV}$ . <sup>d</sup> Estimated from the absorption edge.



**Fig. 3** Transfer characteristics of **1a**- (a) and **1b**- (b) based FETs at a source–drain bias of  $V_{SD} = -60$  V.

**Table 2** FET characteristics of **1a** and **1b**

Compound	$\mu_{\text{sat}}/\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	On/off ratio
<b>1a</b>	$1.0 \times 10^{-2}$	$10^5$
<b>1b</b>	$1.0 \times 10^{-3}$	$10^5$

packed lamellar structure. A further cause might be the lower concentration of the chromophore core. In these comparisons it has to be taken into account that **1a** and **1b** are deposited from different solutions on non-identical transistor substrate configurations.

From the transfer characteristics of **1b** (Fig. 3(b)) a threshold voltage of  $-35$  V and an on/off ratio of  $10^5$  are extracted (Table 2). However, the observed output characteristics (ESI†) indicate severe charge trapping at the semiconductor–dielectric interface or at the macroscopic domain boundaries as observed for **1a**.<sup>12</sup> For further FET optimization, various additional solution processing techniques are in the focus of our interest.

In summary, we have developed a facile synthesis of BBT with and without alkyl substitution. The synthesis utilized a super-acid induced ring closure reaction to fuse two easily prepared synthons. Our preliminary studies revealed better performance of solution processed OFETs in comparison to devices prepared by PVD. Further synthetic design of novel related conjugated oligomers with more thiophene rings parallel with device optimization with regard to the high threshold voltage are currently underway in our laboratory.

This work was supported by EU project NAIMO (NMP4-CT-2004-500355).

## Notes and references

§ *Crystal data for 1a and 1b*:  $\text{C}_{18}\text{H}_{10}\text{S}_2$  **1a**:  $M = 290.41$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.4941(5)$  Å,  $b = 5.9036(4)$  Å,  $c = 11.5824(5)$  Å,  $\beta = 102.94(0)^\circ$ ,  $V = 632.71(20)$  Å<sup>3</sup>,  $Z = 2$ . The structure was refined to a final residual  $wR = 0.0387$ .  $\text{C}_{26}\text{H}_{26}\text{S}_2$  **1b**:  $M = 402.62$ , triclinic, space group  $P\bar{1}$ ,  $a = 4.5840(4)$  Å,  $b = 9.2230(5)$  Å,  $c = 12.4880(5)$  Å,  $\alpha = 89.8540(12)^\circ$ ,  $\beta = 79.5940(13)^\circ$ ,  $\gamma = 79.1590(13)^\circ$ ,  $V = 509.75(19)$  Å<sup>3</sup>,  $Z = 1$ . The structure was refined to a final residual  $wR = 0.0565$ . CCDC 667690 and 667691. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717608b

- (a) Y.-Y. Lin, D. J. Gundlach, S. F. Nelson and T. N. Jackson, *IEEE Electron Device Lett.*, 1997, **18**, 606; (b) S. F. Nelson, Y.-Y. Lin, D. J. Gundlach and T. N. Jackson, *Appl. Phys. Lett.*, 1998, **72**, 1854.
- C. Pannemann, T. Diekmann and U. Hilleringmann, *J. Mater. Res.*, 2004, **19**, 1999.
- (a) P. Herwig and K. Müllen, *Adv. Mater.*, 1999, **11**, 480; (b) M. L. Tang, T. Okamoto and Z. Bao, *J. Am. Chem. Soc.*, 2006, **128**, 16002.
- (a) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J.-L. Brédas, *Chem. Rev.*, 2007, **107**, 926; (b) K. Takimiya, Y. Kunugi, Y. Konda, N. Niihara and T. Otsubo, *J. Am. Chem. Soc.*, 2004, **126**, 5084; (c) K. Takimiya, H. Ebata, K. Sakamoto, T. Izawa, T. Otsubo and Y. Kunugi, *J. Am. Chem. Soc.*, 2006, **128**, 12604; (d) K. Takimiya, Y. Kunugi, Y. Konda, H. Ebata, Y. Toyoshima and T. Otsubo, *J. Am. Chem. Soc.*, 2006, **128**, 3044; (e) T. Yamamoto and K. Takimiya, *J. Am. Chem. Soc.*, 2007, **129**, 2224.
- (a) L. J. Pandya, G. N. Pillai and B. D. Tilak, *J. Sci. Indian Res.*, 1959, **B18**, 198; (b) M. Ahmed, J. Ashby, M. Ayad and O. Meth-Cohn, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1099.
- Very recently, the first OFET based on PVD fabricated BBT has been published during our preparation of this contribution, which reported a FET mobility of  $2.4 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and an on/off ratio of  $10^6$ . Interestingly, our group got the same compound with much simpler method and similar OFET performance through a solution processing technique: H. Ebata, E. Miyazaki, T. Yamamoto and K. Takimiya, *Org. Lett.*, 2007, **9**, 4499.
- A. Haryono, K. Miyatake, J. Natori and E. Tsuchida, *Macromolecules*, 1999, **32**, 3146.
- (a) H. Sirringhaus, R. H. Friend, C. Wang, J. Leuninger and K. Müllen, *J. Mater. Chem.*, 1999, **9**, 2095; (b) J. Leuninger, S. Trimpin, H.-J. Räder and K. Müllen, *Macromol. Chem. Phys.*, 2001, **202**, 2832.
- The structure and purity of **1a** and **1b** are further confirmed by <sup>1</sup>H, <sup>13</sup>C NMR and mass spectrometry as well as elemental analysis (ESI†).
- M. D. Curtis, J. Cao and J. W. Kampf, *J. Am. Chem. Soc.*, 2004, **126**, 4318.
- W. Wang, T. Lee and M. A. Reed, *Phys. Rev. B*, 2003, **68**, 035416.
- G. Horowitz, *Adv. Funct. Mater.*, 2003, **13**, 53.