ORGANIC
LETTERS

2009
Vol. 11, No. 16
3658−3661

2,8- and 2,9-Diboryltetracenes as Useful Building Blocks for Extended π-Conjugated Tetracenes

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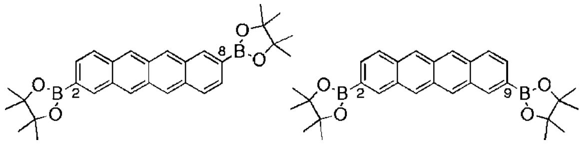
Received June 23, 2009

ABSTRACT



Ir-catalyzed direct diborylation of tetracene gave a 1:1 mixture of 2,8- and 2,9-bis[(pinacolato)boryl]tetracenes, which were separated by recrystallization. These diboryltetracenes are useful building blocks for the regiospecific synthesis of extended π-conjugated tetracenes directed to semiconductors for organic field-effect transistors (OFETs). Syntheses of thiophene−tetracene−thiophene, thiophene−tetracene−bithiophene−tetracene−thiophene, and thiophene−tetracene−anthracene−tetracene−thiophene π-systems have been achieved on the basis of the 2,8- and 2,9-diboryltetracenes.

Tetracene and its derivatives such as rubrene are promising candidates for p-type semiconductors for organic field-effect transistors (OFETs).[1−4] As an extended π-system, higher acenes (pentacene, hexacene, heptacene, etc.) significantly reduce the HOMO−LUMO energy gap,[5] and it is expected that they would enhance the intermolecular overlap of π-orbitals in the solid state and lead to higher hole mobilities.[1] However, higher acenes are very insoluble and become unstable in air and/or light with extension of linearly annelated benzene rings.[1,6] As another extended π-conjugated system, the oligomerization or π-extended functionalization of small acenes such as anthracene and tetracene would also be an effective approach to semiconductors for OFETs[7−10] because this approach would alleviate chemical instability of the molecules by avoiding excessive reduction of the

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(1) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048. (b) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452–483.

(2) (a) Gundlach, D. J.; Nichols, J. A.; Zhou, L.; Jackson, T. N. *Appl. Phys. Lett.* **2002**, *80*, 2925–2927. (b) Goldmann, G.; Haas, S.; Krellner, C.; Pernstich, K. P.; Gundlach, D. J.; Batlogg, B. *J. Appl. Phys.* **2004**, *96*, 2080–2086.

(3) Moon, H.; Zeis, R.; Borkent, E.-J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322–15323.

(4) (a) Podzorov, V.; Menard, E.; Borissov, A.; Kiryukhin, V.; Rogers, J. A.; Gershenson, M. E. *Phys. Rev. Lett.* **2004**, *93*, 086602−1-4. (b) Takeya, J.; Yamagishi, M.; Tominari, Y.; Hirahara, R.; Nakazawa, Y.; Nishikawa, T.; Kawase, T.; Shimoda, T.; Ogawa, S. *Appl. Phys. Lett.* **2007**, *90*, 102120−1-3.

(5) (a) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. *J. Am. Chem. Soc.* **2004**, *126*, 7416–7417. (b) Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643–3646. (c) Norton, J. E.; Houk, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 4162–4163.

(6) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P *J. Am. Chem. Soc.* **2008**, *130*, 16274–16286.

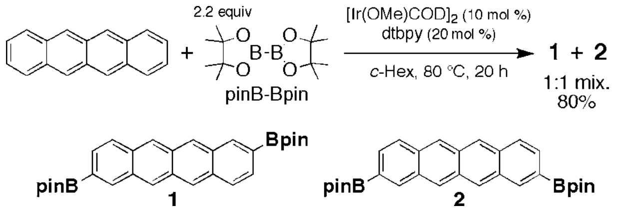
(7) (a) Hodge, P.; Power, G. A.; Rabjohns, M. A. *Chem. Commun.* **1997**, 73–74. (b) Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1159–1162. (c) Cui, W.; Zhang, X.; Jiang, X.; Tian, H.; Yan, D.; Geng, Y.; Jing, X.; Wang, F. *Org. Lett.* **2006**, *8*, 785–788.

10.1021/ol901420p CCC: $40.75

HOMO−LUMO energy gap[5] and could prevent herringbone packing by increasing the ratio of π-faced carbon atoms to π-edged hydrogen atoms.[11] However, selective difunctionalization of tetracene at the 2,8- and 2,9-positions has not been achieved so far.[12] Marder et al. reported Ir-catalyzed direct diborylation of naphthalene at the 2,6- and 2,7-positions.[13] Here we report the Ir-catalyzed direct diborylation of tetracene to produce 2,8- and 2,9-diboryltetracenes **1** and **2**, which are useful building blocks for the regiospecific synthesis of extended π-conjugated tetracenes directed to semiconductors for OFETs. We also describe the synthesis of several types on the basis of **1** and **2**.

The reaction of tetracene with 2.2 equiv of bis(pinacolato)diboron (pinB-Bpin) in the presence of $[Ir(OMe)(COD)]_2$ (10 mol %) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy, 20 mol %) in cyclohexane at 80 °C for 20 h under Ar in the dark gave a 1:1 mixture of 2,8- and 2,9-bis[(pinacolato)boryl]tetracenes **1** and **2** in 80% yield (Scheme 1). Recrystallization of a 1:1 mixture of **1** and **2** from hot *p*-xylene gave pure **2**, and then recrystallization of the **1**-rich mixture from hot toluene−hexane yielded pure **1**. The ^{1}H NMR spectra of both products showed highly symmetrical structures,[14] suggesting the diborylation of tetracene at either the 2,8- or 2,9-positions. The ^{13}C NMR spectra revealed the positions of diborylation of tetracene, wherein **1** and **2** exhibited eight and nine aromatic signals, respectively (carbon attached to boron was not observed).[13,14] The ^{1}H−^{13}C COSY spectra also supported the structures of **1** and **2**.[14] Finally, the molecular structure of **2** was confirmed by a single-crystal X-ray diffraction analysis (Figure 1).[14] The UV−vis spectra of **1** and **2** in CH_2Cl_2 showed absorption maxima (λ_{max}) at 490 nm in both cases, which is red-shifted by 16 nm relative to λ_{max} of tetracene.[14] The TG-DTA analysis of **1** and **2** indicated that both begin to sublime at 263 °C without decomposition.[14]

Scheme 1. Ir-Catalyzed Diborylation of Tetracene To Form **1** and **2**



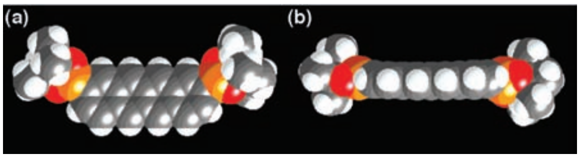
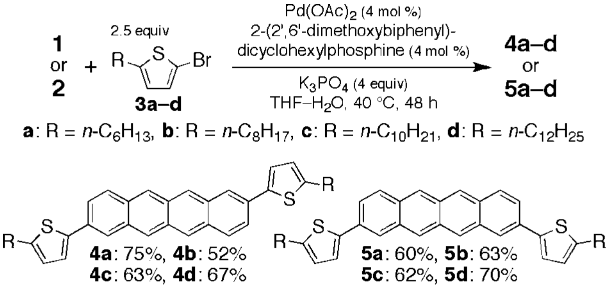


Figure 1. X-ray crystal structure of **2**: (a) front and (b) side views. One of two Bpin groups is disordered.

2,8- and 2,9-diboryltetracenes **1** and **2** are useful building blocks for the regiospecific synthesis of extended π-conjugated tetracenes. The Suzuki−Miyaura cross-coupling reaction of **1** or **2** with 2.5 equiv of 2-bromo-5-alkylthiophenes **3a**−**d** (**a**: R = n-C_6H_{13}, **b**: n-C_8H_{17}, **c**: n-$C_{10}H_{21}$, **d**: n-$C_{12}H_{25}$)[15,16] gave 2,8- or 2,9-bis(5′-alkylthiophen-2′-yl)tetracenes **4a**−**d** or **5a**−**d**, respectively, in moderate to good yields (Scheme 2). The bis(alkylthienyl)tetracenes **4** and **5** are scarcely soluble in $CHCl_3$ and toluene (<0.1 mg/mL at room temperature) and modestly soluble in 1,2,4-trichlorobenzene or hot 1,1,2,2-tetrachloroethane. Compounds **4** and **5** are stable under air without light, but under both air and

Scheme 2. Synthesis of Dithienyltetracenes **4** and **5**



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(8) (a) Meng, H.; Sun, F.; Goldfinger, M. B.; Jaycox, G. D.; Li, Z.; Marshall, W. J.; Blackman, G. S. *J. Am. Chem. Soc.* **2005**, *127*, 2406–2407. (b) Meng, H.; Sun, F.; Goldfinger, M. B.; Gao, F.; Londono, D. J.; Marshall, W. J.; Blackman, G. S.; Dobbs, K. D.; Keys, D. E. *J. Am. Chem. Soc.* **2006**, *128*, 9304–9305. (c) Park, J.-H.; Chung, D. S.; Park, J.-W.; Ahn, T.; Kong, H.; Jung, Y. K.; Lee, J.; Yi, M. H.; Park, C. E.; Kwon, S.-K.; Shim, H.-K. *Org. Lett.* **2007**, *9*, 2573–2576.

(9) Merlo, J. A.; Newman, C. R.; Gerlach, C. P.; Kelley, T. W.; Muyres, D. V.; Fritz, S. E.; Toney, M. F.; Frisbie, C. D. *J. Am. Chem. Soc.* **2005**, *127*, 3997–4009.

(10) (a) Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2007**, *129*, 10308–10309. (b) Lehnherr, D.; Gao, J.; Hegmann, F. A.; Tykwinski, R. R. *Org. Lett.* **2008**, *10*, 4779–4782.

(11) (a) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989; Chapter 4. (b) Kobayashi, K.; Shimaoka, R.; Kawahata, M.; Yamanaka, M.; Yamaguchi, K. *Org. Lett.* **2006**, *8*, 2385–2388, and references cited therein.

(12) For difunctionalized tetracenes at other positions except for the 2,8- and 2,9-positions, see ref 3 and: (a) Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2003**, *5*, 4245–4248. (b) Tulevski, G. S.; Miao, Q.; Fukuto, M.; Abram, R.; Ocko, B.; Pindak, R.; Steigerwald, M. L.; Kagan, C. R.; Nuckolls, C. *J. Am. Chem. Soc.* **2004**, *126*, 15048–15050. (c) Reichwagen, J.; Hopf, H.; Del Guerzo, A.; Belin, C.; Bouas-Laurent, H.; Desvergne, J.-P. *Org. Lett.* **2005**, *7*, 971–974. (d) Chen, Z.; Muller, P.; Swager, T. M. *Org. Lett.* **2006**, *8*, 273–276. (e) Liang, Z.; Zhao, W.; Wang, S.; Tang, Q.; Lam, S.-C.; Miao, Q. *Org. Lett.* **2008**, *10*, 2007–2010.

(13) (a) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172–2174. (b) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390–391.

(14) See the Supporting Information.

(15) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696.

(16) van Breemen, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M.; Setayesh, S.; Hardeman, W. M.; Martin, C. A.; de Leeuw, D. M.; Valeton, J. J. P.; Bastiaansen, C. W. M.; Broer, D. J.; Popa-Merticaru, A. R.; Meskers, S. C. J. *J. Am. Chem. Soc.* **2006**, *128*, 2336–2345.

room light, **4** and **5** in solution gradually decomposed to a complex mixture. The TG-DTA analysis showed that the melting points of **4a**−**d** are ca. 20 °C higher than those of **5a**−**d**, respectively.[14]

In the UV−vis spectra, λ_{max} of **4b** and **5b** in 1,2,4-trichlorobenzene were red-shifted by 35 and 30 nm relative to λ_{max} of tetracene, respectively, because of extension of the π-conjugation (Figure 2a). DFT calculations (B3LYP/6-31G(d) level) of **4** and **5** (R = CH_3) showed that the HOMO is delocalized moderately over the tetracene and thiophene rings (Figure 3). The HOMO and LUMO energy levels were −4.742 and −2.192 eV for **4** and −4.754 and −2.188 eV for **5**. This result indicates that the HOMO energies of **4** and **5** are slightly higher than the calculated value of tetracene (−4.86 eV) and the LUMO energies of **4** and **5** are slightly lower than that of tetracene (−2.08 eV).[5c] The HOMO−LUMO energy gap decreases in the order tetracene > **5** ≥ **4**.

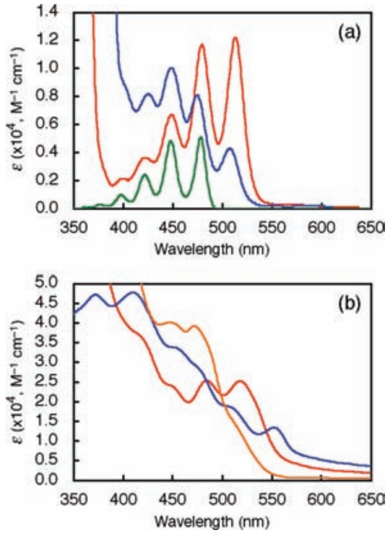

Figure 2. UV−vis spectra of extended π-conjugated tetracenes in 1,2,4-trichlorobenzene: (a) **4b** (red), **5b** (blue), and tetracene (green); (b) **8** (red), **9** (blue), and **10** (orange).

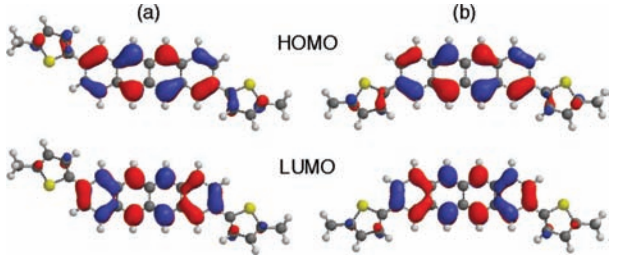

Figure 3. HOMO−LUMO diagrams of (a) **4** (R = CH_3) and (b) **5** (R = CH_3).

Meng and co-workers reported that 2,6-bis(5′-hexylthiophen-2′-yl)anthracene exhibits good OFET properties.[8a] Compound **4a** is the exactly extended π-conjugated analogue of this anthracene derivative. OFET devices of **4b** and **5b** with a bottom-contact configuration were fabricated on a SiO_2/n-doped Si substrate and source/drain gold electrodes by high-vacuum evaporation at a substrate deposition temperature of room temperature as a preliminary study. The OFET devices showed the well-resolved output and transfer characteristics (Figure 4).[14] The hole mobilities calculated in the saturation regime were 3×10^{-2} cm^2 V^{-1} s^{-1} for **4b** and 2×10^{-2} cm^2 V^{-1} s^{-1} for **5b**. The current on/off ratios of $>1 \times 10^3$ and $>1 \times 10^5$ and threshold voltages of −2.2 and −16.5 V were observed for OFETs with **4b** and **5b**, respectively.

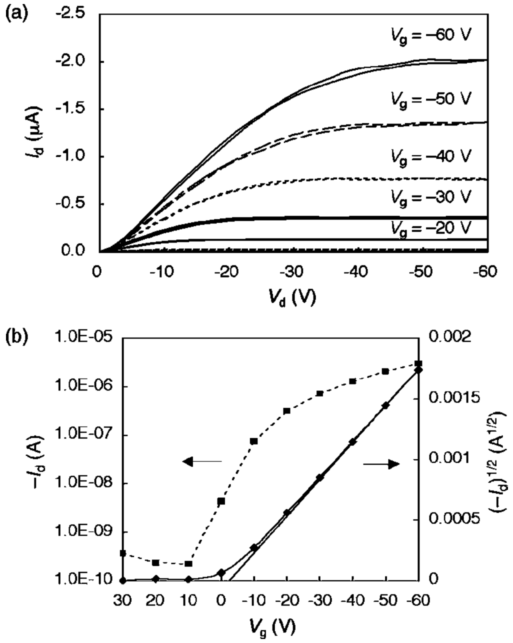

Figure 4. *I*−*V* characteristics of a bottom-contact OFET device using **4b** semiconductor: (a) output curves at different gate voltages; (b) transfer curve in saturated regime at constant source-drain voltage of −40 V and square root of the absolute value of the drain current as a function of gate voltage.

When the coupling of **1** or **2** with 1 equiv of **3d** was carried out for 2 h (other conditions were the same as those shown in Scheme 2), 2-boryl-8-thienyltetracene **6** or its 2,9-isomer **7** were obtained in moderate yields, respectively (Figure 5),[14] which can also serve as other building blocks for the synthesis of extended π-conjugated tetracenes. The coupling reaction of 2.2 equiv of **6** or **7** with **11**[17] at 60 °C for 30 h gave the thiophene−tetracene−bithiophene−tetracene−thiophene π-system **8** or **9** in good yields, respectively (Figure 5).[14] The thiophene−tetracene−anthracene−tetracene−thiophene π-system **10** was also synthesized from **7** and **12**.[8c,14] The UV−vis spectra of **8**, **9**, and **10** in 1,2,4-

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[17] Zrig, S.; Koeckelberghs, G.; Verbiest, T.; Andrioletti, B.; Rose, E.; Persoons, A.; Asselberghs, I.; Clays, K. *J. Org. Chem.* **2007**, *72*, 5855–5858.

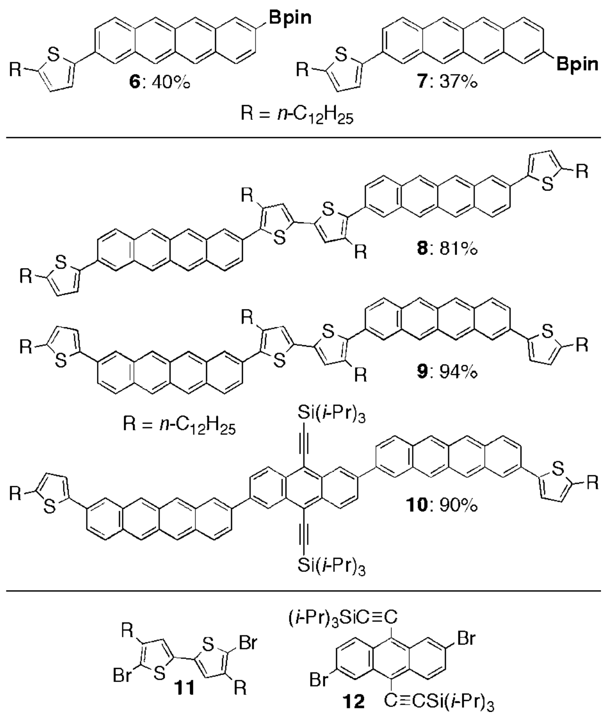

Figure 5. Structures of coupling products **6**−**10**.

trichlorobenzene are shown in Figure 2b. Their absorption bands are greatly broadened compared with those of the thiophene−tetracene−thiophene π-systems **4b** and **5b** because of extension of the π-conjugation (Figure 2a vs b). The λ_{max} of these compounds in 1,2,4-trichlorobenzene were red-shifted in the order tetracene (478 nm) < **6** (494 nm) < **7** (502 nm) < **5b** (508 nm) < **4b** (513 nm) < **8** (518 nm) ≤ **10** (519 nm) < **9** (552 nm). This result indicates that the HOMO−LUMO energy gap decreases in this order and that the degree of π-conjugated expansion of tetracene depends on a combination of the connective position between aromatics (2,8- or 2,9-position) and the types of aromatics.

Oligomer **10** has moderate solubility in $CDCl_3$ (ca. 4 mM), allowing us to study the self-association behavior of **10**. The ^1H NMR of **10** showed that all aromatic signals of **10** were shifted upfield upon increasing the concentration, indicating self $\pi-\pi$ stacking of **10**.[14,18] The self-association constant of **10** was estimated to be $K_a = 54\ M^{-1}$ in $CDCl_3$ at 298 K.

In summary, we have shown the synthesis of 2,8- and 2,9-diboryltetracenes **1** and **2**, which are useful building blocks for the regiospecific synthesis of extended π-conjugated tetracenes directed to semiconductors for OFETs. We have demonstrated the syntheses of thiophene−tetracene−thiophene, thiophene−tetracene−bithiophene−tetracene−thiophene, and thiophene−tetracene−anthracene−tetracene−thiophene π-systems by cross-coupling reactions using **1** and **2**. Studies on the preparation of thin films and the OFET properties of these extended π-conjugated tetracenes are currently in progress.

Acknowledgment. This work was supported in part by PRESTO, JST.

Supporting Information Available: Additional data and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OL901420P

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(18) Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019–1027.