

A Planarized Triphenylborane Mesogen: Discotic Liquid Crystals with Ambipolar Charge-Carrier Transport Properties**

Tomokatsu Kushida, Ayumi Shuto, Masafumi Yoshio,* Takashi Kato, and Shigehiro Yamaguchi*

Abstract: A discotic liquid-crystalline (LC) material, consisting of a planarized triphenylborane mesogen, was synthesized. X-ray diffraction analysis confirmed that this compound forms a hexagonal columnar LC phase with an interfacial distance of 3.57 Å between the discs. At ambient temperature, this boron-centered discotic liquid crystal exhibited ambipolar carrier transport properties with electron and hole mobility values of approximately 10^{-3} and $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

Triarylboranes are attractive building blocks for organic electronic materials,^[1] and the extended π -conjugation through the vacant p orbital of the boron atom imparts these compounds with electron-accepting and Lewis acidic character. A variety of fascinating triarylborane-based materials have been developed,^[2] and their diverse applications arch from electron-transporting materials^[3] over nonlinear optical and two-photon absorption materials^[4] to anion sensors.^[5] In this area of chemistry, stability is often an issue of concern, as the boron center exhibits high reactivity towards nucleophiles, such as water. Even though the introduction of bulky substituents generally leads to a kinetic stabilization of the reactive boron center,^[3–6] the steric bulk simultaneously hampers intermolecular interactions in the condensed phase. Based on this notion,

the formation of infinitely columnar structures, π stacked in a face-to-face fashion, has been considered difficult to accomplish with triarylborane synthons.

In this context, we have recently proposed structural constraint as a novel design approach for the stabilization of triarylboranes. Enforced planar triphenylboranes can be generated by the incorporation of three methylene bridges at the *ortho*-position of the phenyl groups (Figure 1 a). The fixation of three benzene rings in such a coplanar fashion resulted in substantial stability of these planar triphenylboranes towards atmospheric air and moisture, and it was even

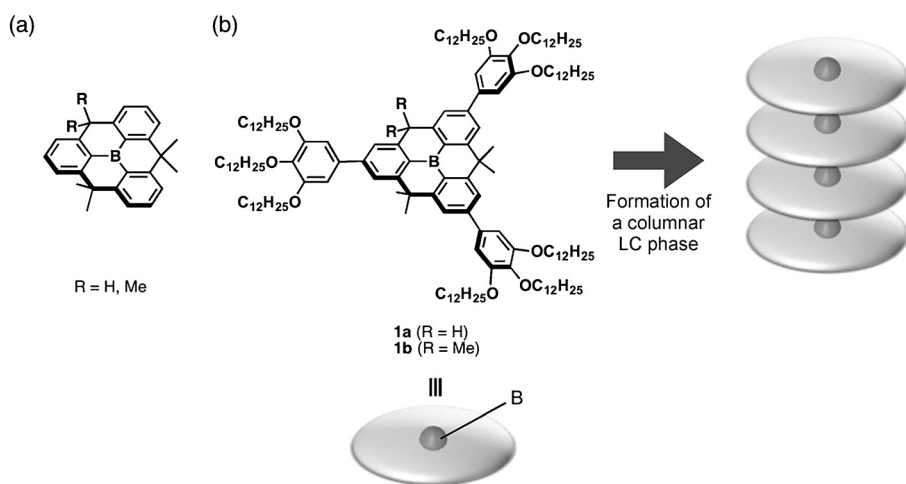


Figure 1. Structural formula of a) planarized triphenylboranes and b) trigonally π -extended derivatives **1a,b**.

[*] Dr. T. Kushida, A. Shuto, Prof. Dr. S. Yamaguchi
Department of Chemistry, Graduate School of Science and Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University
Furo, Chikusa, Nagoya 464-8602 (Japan)
E-mail: yamaguchi@chem.nagoya-u.ac.jp

Prof. Dr. M. Yoshio, Prof. Dr. T. Kato
Department of Chemistry and Biotechnology
School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: yoshio@chembio.t.u-tokyo.ac.jp

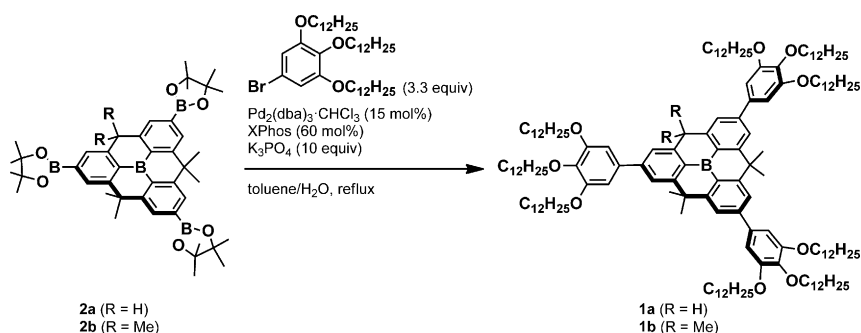
[**] This work was supported by CREST, JST, for S.Y. and Grants-in-Aid for Scientific Research on Innovative Area (Stimuli-responsive Chemical Species, no. 24109007 for S.Y. and no. 25109513 for M.Y.) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201502678>.

possible to purify these compounds by column chromatography on silica gel despite the absence of any steric protection around the boron center.^[7] The concept of planarized triphenylboranes could moreover be applied to the generation of a variety of highly intriguing compounds, for example, borataanthracenes,^[8] boron-centered radical anions,^[9] boracyclophanes,^[10] and boron-based emissive materials with large Stokes shifts.^[11] Planarized triphenylboranes were also successfully employed as building blocks for the electron-transporting materials in organic light-emitting diodes (OLEDs).^[12] But even though these highly planar triphenylboranes lack sterically bulky substituents in the vertical direction, their columnar alignment in the condensed phase still remains to be realized.^[13] We envisioned that such an alignment may be achieved in the liquid-crystalline (LC) phase (Figure 1b), as liquid crystals consisting of a planar disc-shaped mesogen often form columnar LC phases, in

which the core π -skeletons are stacked. Such discotic LC π -electron systems represent an attractive research target, as they should be able to serve as the semiconducting soft materials.^[14] In addition, theoretical calculations predicted that planarized triphenylboranes should constitute promising candidates for ambipolar semiconducting materials in organic electronics.^[15] Herein, we report the synthesis and characterization of LC planarized triphenylboranes **1**, bearing nine long alkoxy chains at the aryl periphery. The carrier mobilities of **1** in the LC phase was examined by time-of-flight (TOF) methods, which revealed that these new LC materials form hexagonal columnar phases at ambient temperature and exhibit ambipolar carrier transport properties.

Previously, we reported the synthesis of planarized triphenylborane **2a**, bearing three Bpin groups, which serves as a useful precursor for the introduction of three aryl groups in a trigonally π -extended fashion.^[11] With the triphenylborane precursors **2a** ($R = H$) and **2b** ($R = Me$) in hand, we were able to synthesize 3,4,5-tridodecyloxyphenyl-substituted **1a** (40%) and **1b** (27%) by Suzuki–Miyaura cross-coupling reactions using the corresponding aryl bromides (Scheme 1). Similar to the previously reported planarized triphenylboranes, compounds **1a,b** did not exhibit any signs of deterioration upon exposure to air.



Scheme 1. Synthesis of 3,4,5-tridodecyloxyphenyl-substituted planarized triphenylboranes **1a,b** (dba = dibenzylideneacetone, XPhos = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl).

In contrast to fully methylated **1b**, which did not form a mesophase, the formation of an LC phase was observed for sterically less hindered **1a**. Differential scanning calorimetry (DSC) measurements of **1b** revealed the presence of a phase transition between a solid and an isotropic liquid at 11.2 °C upon cooling (Figure S10 in the Supporting Information). Conversely, two exothermic peaks (80.8/3.3 °C) were observed for **1a** upon cooling from the melted isotropic

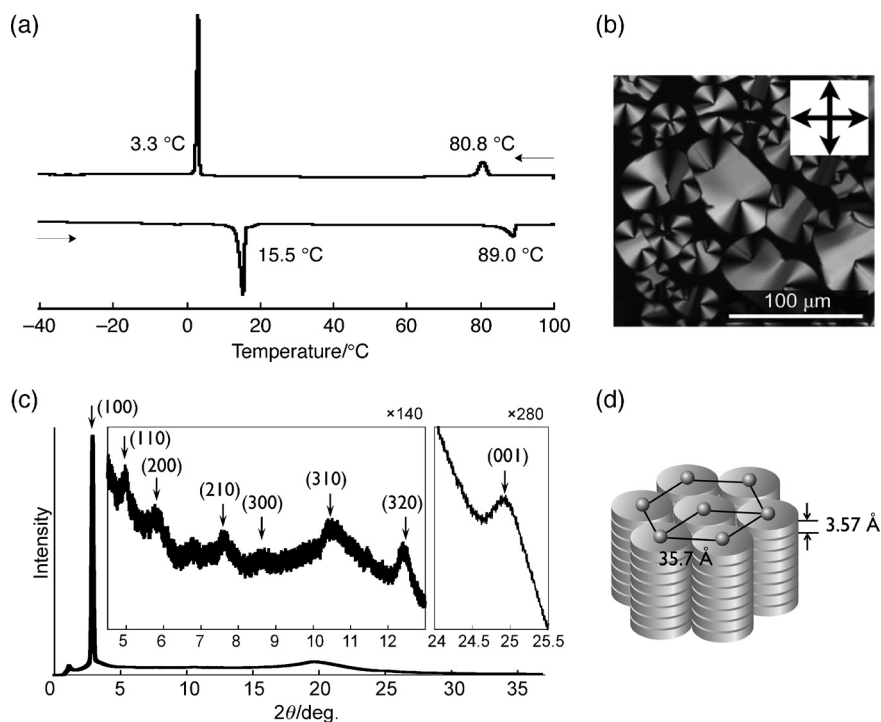


Figure 2. a) Differential scanning calorimetry trace of **1a** (heating/cooling rate: 1 °C min⁻¹). b) Polarized optical microscope image of **1a** at 70 °C upon cooling from the isotropic liquid. The inset indicates the directions of polarizer and analyzer. c) X-ray diffraction pattern of **1a** at ambient temperature after cooling from the isotropic liquid. d) Schematic illustration of the hexagonal columnar phase of **1a**.

liquid (Figure 2a), which suggests the formation of an LC phase in this temperature range. And indeed, a fan-shaped texture was observed under a polarized optical microscope at 70 °C upon cooling from the isotropic liquid (Figure 2b).

We characterized the LC phase of **1a** by X-ray diffraction (XRD) analysis (Figure 2c), and the XRD pattern of **1a** at room temperature after cooling from the isotropic liquid exhibited an intense peak at $2\theta = 2.86^\circ$, which was assigned to the reflection from the (100) plane. In the low angle region, seven peaks with d -spacing values in the ratio of 1:1/ $\sqrt{3}$:1/2:1/ $\sqrt{7}$:1/3:1/ $\sqrt{13}$:1/ $\sqrt{19}$ were observed. Based on these ratios, the seven peaks were assigned to the reflections of the (100), (110), (200), (210), (300), (310), and (320) planes (Table S1 in the Supporting Information). The LC phase of **1a** is accordingly best described as a hexagonal columnar phase (Col_h), exhibiting a lattice parameter a (i.e. the distance between boron centers in neighboring columns) of 35.7 Å, and this assignment is also consistent with the reciprocal lattice analysis (Figure S11 in the Supporting Information). The reflection arising from the one-dimensional order, that is, the (001) plane, was observed at $2\theta = 24.92^\circ$, which allows the determination of the lattice parameter c (i.e. the distance between the discs within a column) to

3.57 Å, indicative of a close π -stacking of the discotic mesogens. The number (n) of molecules per unit cell in a hexagonal lattice can be determined using the following equation: $n = \sqrt{3} N_A a^2 c \rho / 2M$, where N_A is the Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), ρ refers to the density (ca. 1 g cm^{-3}), and M represents the molecular weight ($2221.47 \text{ g mol}^{-1}$).^[16] An n value of 1.07 was determined for the Col_h phase of **1a**, suggesting the formation of a columnar structure in a monomeric fashion, which allows the hexagonal columnar phase of discotic mesogen **1a** to be schematically drawn as shown in Figure 2d.

A comparison of the photophysical properties of **1a** in solution (THF) and in the LC phase provided some insight into the electronic interaction in the LC phase (Figure 3a). In

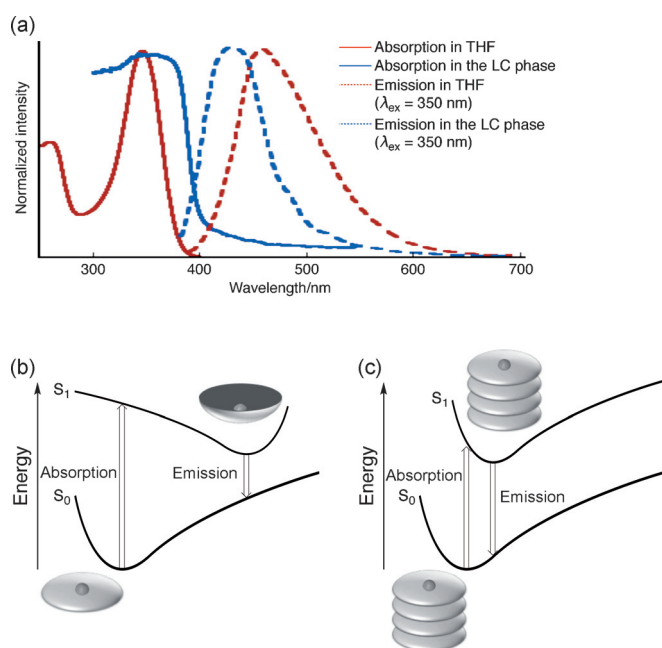


Figure 3. a) Absorption and emission spectra of **1a** in THF and the LC phase. Schematic illustrations of the excited state dynamics of **1a** in b) solution and c) the LC phase.

THF, **1a** exhibited an absorption maximum at 346 nm ($\epsilon = 6.62 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and an intense blue emission ($\lambda_{\text{em}} = 457 \text{ nm}$) with a remarkably high fluorescence quantum yield close to unity ($\Phi_{\text{em}} = 0.99$). Notably, despite its planar structure, a Stokes shift of 7020 cm^{-1} was observed. A similarly large Stokes shift was observed for a previously reported planarized triphenylborane with tris(4-hexyloxyphenyl) substituents. Taking the results and conclusions of this previous study, regarding the origin of the large Stokes shift, into account,^[11] the emission of **1a** is most likely due to a distorted bowl-shaped conformation of the lowest excited singlet state S_1 (Figure 3b). The absorption spectrum in the LC phase, on the other hand, was bathochromically shifted relative to that in THF, which suggests electronic interaction of the π -skeletons in the columnar π -stacked ground

state S_0 (Figure 3c). In stark contrast, the maximum wavelength of the emission ($\lambda_{\text{em}} = 427 \text{ nm}$) in the LC phase was blue-shifted by 30 nm relative to that in THF while maintaining a high quantum yield ($\Phi_{\text{em}} = 0.61$). The hypsochromic shift can be rationalized in terms of a suppression of the structural deformation in the LC phase from the planar to the bowl shape (Figure 3c). All these results are consistent with the results from the structural XRD analysis and suggest that compound **1a** is densely π -stacked in the columnar LC phase.

The formation of columnar π -stacks consisting of **1a** encouraged us to investigate the charge carrier transport properties in the LC phase. For that purpose, we measured the hole and electron carrier mobilities of **1a** in the LC phase by the TOF method.^[17] Compound **1a** was filled in electrode cells of indium-tin-oxide (ITO; gap: $4 \mu\text{m}$), in which the hexagonal columns were vertically aligned on the surface of the ITO substrate. The transient photocurrent curves at 40°C for holes and electrons are shown in Figure 4. Non-dispersive transient photocurrent signals were obtained for the hole transport, and the hole transit time was observed to decrease with increasing strength of the applied electric field. In contrast, dispersive photocurrent curves were observed for the electrons, probably due to electron trapping by the Lewis acidic boron atom at the center of the discotic mesogen. Transit times for the hole transport were determined on the basis of linear plots of the transient photocurrent curves (Figure 4a). A hole mobility of $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was calculated, and this value was not affected by a variation of the applied electric field (Figure S13 in the Supporting Information). The electron mobility (ca. $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was estimated by using a value of $4 \times 10^{-6} \text{ s}$ for the transit time of electrons, which was obtained from the double-logarithmic plots of the photocurrent curves shown in the inset of Figure 4b. Although the determination of electron mobilities is nontrivial owing to the dispersive transient nature of the photocurrent signals, it can be concluded that compound **1a** exhibited ambipolar charge carrier transport properties.

In summary, we synthesized planarized triphenylboranes **1a,b**, which bear nine long alkoxy chains. DSC and XRD measurements revealed that disc-shaped triphenylborane **1a** forms a closely π -stacked hexagonal columnar LC phase at

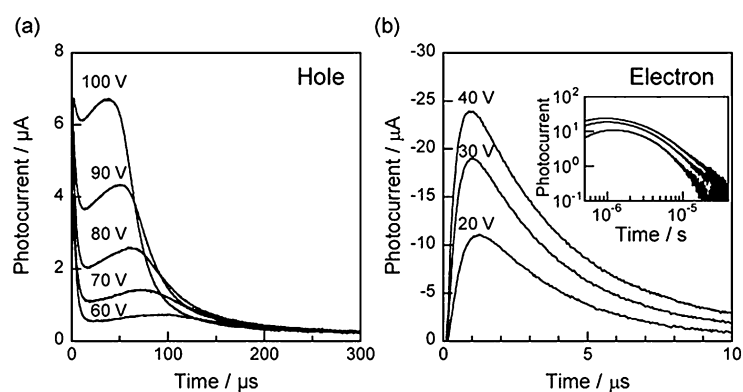


Figure 4. Transient photocurrent curves for a) holes and b) electrons in the columnar LC phase of **1a** at 40°C . Inset: the double-logarithmic plots of the photocurrent curves.

room temperature. The examination of the photophysical properties of **1a** supports an electronic interaction of π -skeletons in the LC phase. The LC material based on planarized triphenylborane **1a** showed ambipolar carrier transport properties with hole and electron mobility values of $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and approximately $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. These results should thus provide important guidelines for the design of novel ambipolar semiconducting soft materials.

Keywords: boron · charge carrier transport · liquid crystals · stacking interactions · x-ray diffraction

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 6922–6925
Angew. Chem. **2015**, *127*, 7026–7029

- [1] a) C. D. Entwistle, T. B. Marder, *Angew. Chem. Int. Ed.* **2002**, *41*, 2927; *Angew. Chem.* **2002**, *114*, 3051; b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574; c) S. Yamaguchi, A. Wakamiya, *Pure Appl. Chem.* **2006**, *78*, 1413; d) M. J. D. Bosdet, W. E. Piers, *Can. J. Chem.* **2009**, *87*, 8; e) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985.
- [2] a) W.-L. Jia, D.-R. Bai, T. McCormick, Q.-D. Liu, M. Motala, R.-Y. Wang, C. Seward, Y. Tao, S. Wang, *Chem. Eur. J.* **2004**, *10*, 994; b) W. L. Jia, M. J. Moran, Y.-Y. Yuan, Z. H. Lu, S. Wang, *J. Mater. Chem.* **2005**, *15*, 3326; c) X. Y. Liu, D. R. Bai, S. Wang, *Angew. Chem. Int. Ed.* **2006**, *45*, 5475; *Angew. Chem.* **2006**, *118*, 5601; d) S. K. Møllerup, S. Wang, *Organometallics* **2014**, *33*, 5483; e) C. Hoffend, F. Schödel, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Eur. J.* **2012**, *18*, 15394; f) C. Reus, S. Weidlich, M. Bolte, H.-W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2013**, *135*, 12892; g) C. Hoffend, M. Diefenbach, E. Januszewski, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Dalton Trans.* **2013**, *42*, 13826; h) C. Hoffend, K. Schickedanz, M. Bolte, H.-W. Lerner, M. Wagner, *Tetrahedron* **2013**, *69*, 7073; i) C. Reus, F. Guo, A. John, M. Winhold, H.-W. Lerner, F. Jäkle, M. Wagner, *Macromolecules* **2014**, *47*, 3727; j) P. Chen, F. Jäkle, *J. Am. Chem. Soc.* **2011**, *133*, 20142; k) P. Chen, R. A. Lalancette, F. Jäkle, *Angew. Chem. Int. Ed.* **2012**, *51*, 7994; *Angew. Chem.* **2012**, *124*, 8118; l) L. Weber, V. Werner, M. A. Fox, T. B. Marder, S. Schwedler, A. Brockhinke, H.-G. Stämmler, B. Neumann, *Dalton Trans.* **2009**, 1339; m) L. Weber, D. Eickhoff, T. B. Marder, M. A. Fox, P. J. Low, A. D. Dwyer, D. J. Tozer, S. Schwedler, A. Brockhinke, H.-G. Stämmler, B. Neumann, *Chem. Eur. J.* **2012**, *18*, 1369; n) X. Yin, J. Chen, R. A. Lalancette, T. B. Marder, F. Jäkle, *Angew. Chem. Int. Ed.* **2014**, *53*, 9761; *Angew. Chem.* **2014**, *126*, 9919.
- [3] a) T. Noda, Y. Shirota, *J. Am. Chem. Soc.* **1998**, *120*, 9714; b) Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1; c) Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953; d) D. Tanaka, T. Takeda, T. Chiba, S. Watanabe, J. Kido, *Chem. Lett.* **2007**, *36*, 262; e) D. Tanaka, Y. Agata, T. Takeda, S. Watanabe, J. Kido, *Jpn. J. Appl. Phys.* **2007**, *46*, L117; f) K. Shizu, T. Sato, K. Tanaka, H. Kaji, *Appl. Phys. Lett.* **2010**, *97*, 142111.
- [4] a) Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz, L.-T. Cheng, *J. Chem. Soc. Chem. Commun.* **1990**, 1489; b) M. Lequan, R. M. Lequan, K. C. Ching, *J. Mater. Chem.* **1991**, *1*, 997; c) Z. Yuan, N. J. Taylor, Y. Sun, T. B. Marder, I. D. Williams, L.-T. Cheng, *J. Organomet. Chem.* **1993**, *449*, 27; d) C. Branger, M. Lequan, R. M. Lequan, M. Barzoukas, A. Fort, *J. Mater. Chem.* **1996**, *6*, 555; e) C. Branger, M. Lequan, R. M. Lequan, M. Large, F. Kajzar, *Chem. Phys. Lett.* **1997**, *272*, 265; f) Z. Yuan, J. C. Collings, N. J. Taylor, T. B. Marder, C. Jardin, J.-F. Halet, *J. Solid State Chem.* **2000**, *154*, 5; g) Z.-Q. Liu, Q. Fang, D. Wang, G. Xue, W.-T. Yu, Z.-S. Shao, M.-H. Jiang, *Chem. Commun.* **2002**, 2900; h) Z.-Q. Liu, Q. Fang, D. Wang, D.-X. Cao, G. Xue, W.-T. Yu, H. Lei, *Chem. Eur. J.* **2003**, *9*, 5074; i) Z.-Q. Liu, Q. Fang, D.-X. Cao, D. Wang, G. B. Xu, *Org. Lett.* **2004**, *6*, 2933; j) Z.-Q. Liu, M. Shi, F.-Y. Li, Q. Fang, Z.-H. Chen, T. Yi, C.-H. Huang, *Org. Lett.* **2005**, *7*, 5481; k) M. Charlot, L. Porrès, C. D. Entwistle, A. Beeby, T. B. Marder, M. Blanchard-Desce, *Phys. Chem. Chem. Phys.* **2005**, *7*, 600; l) Z. Yuan, C. D. Entwistle, J. C. Collings, D. Albesa-Jové, A. S. Batsanov, J. A. K. Howard, N. J. Taylor, H. M. Kaiser, D. E. Kaufmann, S.-Y. Poon, W.-Y. Wong, C. Jardin, S. Fathallah, A. Boucekkine, J.-F. Halet, T. B. Marder, *Chem. Eur. J.* **2006**, *12*, 2758; m) J. C. Collings, S.-Y. Poon, C. L. Droumaguet, M. Charlot, C. Katan, L.-O. Pålsson, A. Beeby, J. A. Mosely, H. Kaiser, D. Kaufmann, W.-Y. Wong, M. Blanchard-Desce, T. B. Marder, *Chem. Eur. J.* **2009**, *15*, 198; n) C. D. Entwistle, J. C. Collings, A. Steffen, L.-O. Pålsson, A. Beeby, D. Albesa-Jové, J. M. Burke, A. S. Batsanov, J. A. K. Howard, J. A. Mosely, S.-Y. Poon, W.-Y. Wong, F. Ibersiene, S. Fathallah, A. Boucekkine, J.-F. Halet, T. B. Marder, *J. Mater. Chem.* **2009**, *19*, 7532; o) L. Ji, Q. Fang, M.-S. Yuan, Z.-Q. Liu, Y.-X. Shen, H.-F. Chen, *Org. Lett.* **2010**, *12*, 5192; p) L. Ji, R. M. Edkins, L. J. Sewell, A. Beeby, A. S. Batsanov, K. Fucke, M. Drafz, J. A. K. Howard, O. Moutounet, F. Ibersiene, A. Boucekkine, E. Furet, Z. Liu, J.-F. Halet, C. Katan, T. B. Marder, *Chem. Eur. J.* **2014**, *20*, 13618.
- [5] a) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2001**, *123*, 11372; b) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbaï, *Chem. Rev.* **2010**, *110*, 3958, and references therein.
- [6] a) S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2002**, *124*, 8816; b) A. Wakamiya, K. Mishima, K. Ekawa, S. Yamaguchi, *Chem. Commun.* **2008**, 579; c) L. G. Mercier, W. E. Piers, M. Parvez, *Angew. Chem. Int. Ed.* **2009**, *48*, 6108; *Angew. Chem.* **2009**, *121*, 6224; d) A. Caruso, Jr., M. A. Siegler, J. D. Tovar, *Angew. Chem. Int. Ed.* **2010**, *49*, 4213; *Angew. Chem.* **2010**, *122*, 4309.
- [7] Z. Zhou, A. Wakamiya, T. Kushida, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 4529.
- [8] T. Kushida, Z. Zhou, A. Wakamiya, S. Yamaguchi, *Chem. Commun.* **2012**, 48, 10715.
- [9] T. Kushida, S. Yamaguchi, *Organometallics* **2013**, *32*, 6654.
- [10] T. Kushida, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2013**, *52*, 8054; *Angew. Chem.* **2013**, *125*, 8212.
- [11] T. Kushida, C. Camacho, A. Shuto, S. Irle, M. Muramatsu, T. Katayama, S. Ito, Y. Nagasawa, H. Miyasaka, E. Sakuda, N. Kitamura, Z. Zhou, A. Wakamiya, S. Yamaguchi, *Chem. Sci.* **2014**, *5*, 1296.
- [12] A. Shuto, T. Kushida, T. Fukushima, H. Kaji, S. Yamaguchi, *Org. Lett.* **2013**, *15*, 6234.
- [13] We have recently reported an example, in which a partially fused trinaphthylborane forms a face-to-face π -stacked structure in the crystalline solid state and shows ambipolar charge carrier transport properties, see: K. Matsuo, S. Saito, S. Yamaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 12580.
- [14] a) H. Iino, J. Hanna, *Opto-Electron. Rev.* **2005**, *13*, 295; b) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902; c) M. Funahashi, *Polym. J.* **2009**, *41*, 459.
- [15] T. B. Tai, V. T. T. Huong, M. T. Nguyen, *J. Phys. Chem. C* **2013**, *117*, 14999.
- [16] a) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **2001**, *123*, 1302; b) A. Schaz, E. Valaityte, G. Lattermann, *Liq. Cryst.* **2005**, *32*, 513; c) M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2006**, *128*, 5570.
- [17] a) R. G. Kepler, *Phys. Rev.* **1960**, *119*, 1226; b) M. Funahashi, F. Zhang, N. Tamaoki, *Adv. Mater.* **2007**, *19*, 353.

Received: March 23, 2015

Published online: April 23, 2015