Communications

Intramolecular B–N Coordination as a Scaffold for Electron-Transporting Materials: Synthesis and Properties of Boryl-Substituted Thienylthiazoles**

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The exploration of new and excellent electron-transporting materials is a current topic in the field of organic electronics, including organic light-emitting diodes (OLEDs) and organic thin-film transistors (OTFTs).[1] A crucial issue in their molecular design is the creation of a π-conjugated framework that has a reasonably high electron affinity as well as a suitable solid-state structure for facilitating an efficient carrier transport. The employment of C=N double-bond-containing N-heteroaromatic rings as building units is a widely accepted and effective design because of their intrinsically high electron affinity. In fact, various types of fascinating materials have already been developed along this line.[2–11] We now disclose a new concept for the further structural and electronic modification of N-heteroaromatic ring-based materials by exploiting the Lewis acidity of the boron atom.[12] Thus, our idea is to incorporate boryl groups at the appropriate positions of a nitrogen-containing π-conjugated framework to allow intramolecular coordination from the Lewis basic nitrogen atom to the boron atom, as shown in Figure 1. This interaction between the Lewis acid and Lewis base would not only constrain the π-conjugated framework in a planar fashion,[13] but would also affect the electronic structure by lowering the LUMO level. Therefore, we have designed the (3-boryl-2-thienyl)-2-thiazole **1** as a key building unit. The use of the thienylthiazole skeleton[14] would allow us to achieve regioselective and stepwise metallations at the 5-positions of the thiazole and thiophene rings in **1**, which would be a significant advantage for synthesizing a wide range of compounds derived from this key skeleton.
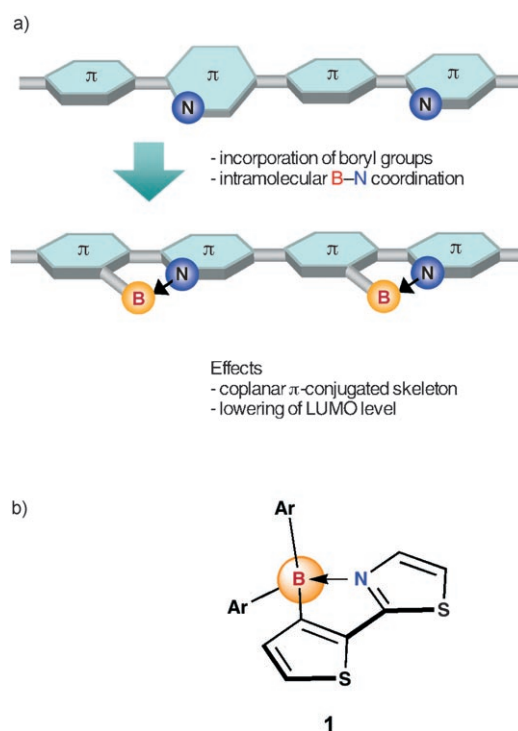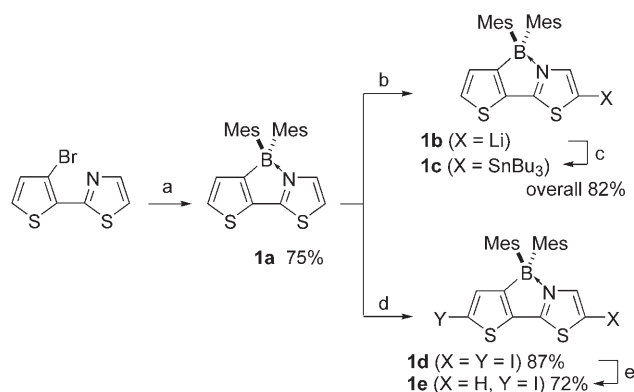

Figure 1. a) Schematic representation of electronic and structural modification of N-heteroaromatic ring-based π-electron systems by intramolecular B–N coordination. b) Boryl-substituted thienylthiazole **1** as a key building unit.

The dimesitylboryl-substituted thienylthiazole **1a** was prepared in 75% yield from (3-bromo-2-thienyl)-2-thiazole by lithiation with *n*BuLi and subsequent treatment with Mes$_2$BF (Mes = 2,4,6-Me$_3$C$_6$H$_2$; Scheme 1). Compound **1a** is stable in air and water and can be purified by column chromatography on silica gel. The X-ray crystal structure analysis of **1a** reveals a B–N bond length of 1.67 Å, thus demonstrating that the intramolecular coordination between the nitrogen atom and the boron atom actually occurs in this skeleton. This coordination constrains the thienylthiazole skeleton in the s-*cis* conformation with a dihedral angle of 7.4°

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Scheme 1. Reagents and conditions: a) *n*BuLi (1 equiv), diethyl ether, −78 °C, then Mes$_2$BF; b) *n*BuLi (1 equiv), THF, −78 °C; c) Bu$_3$SnCl; d) *n*BuLi (2 equiv), THF, −78 °C, then I$_2$; e) *n*BuLi (1 equiv), THF, −78 °C, then H$_2$O.

between the thiophene plane and thiazole plane (see the Supporting Information).[15]

The functionalization of **1a** was examined as shown in Scheme 1. The monolithiation of **1a** with one equivalent of *n*BuLi proceeded regioselectively at the 5-position of the thiazole ring. The resultant monolithiated derivative **1b** was treated with Bu₃SnCl to give the thiazole-monofunctionalized derivative **1c** in 82% yield. The dilithiation of **1a** was achieved by treatment with two equivalents of *n*BuLi, and subsequent treatment with iodine gave the diiodide derivative **1d** in 87% yield. Additionally, the further monolithiation of **1d** with one equivalent of *n*BuLi proceeded at the 5-position of the thiazole ring, and quenching with water afforded the thiophene-monofunctionalized derivative **1e** in 72% yield.

To demonstrate the utility of these functionalized derivatives as precursors for extended π-electron systems, we synthesized a series of regioisomeric dimers, including the head-to-head (H–H), head-to-tail (H–T), and tail-to-tail (T–T) dimers **2**–**4** (Scheme 2), in which the thiophene ring is
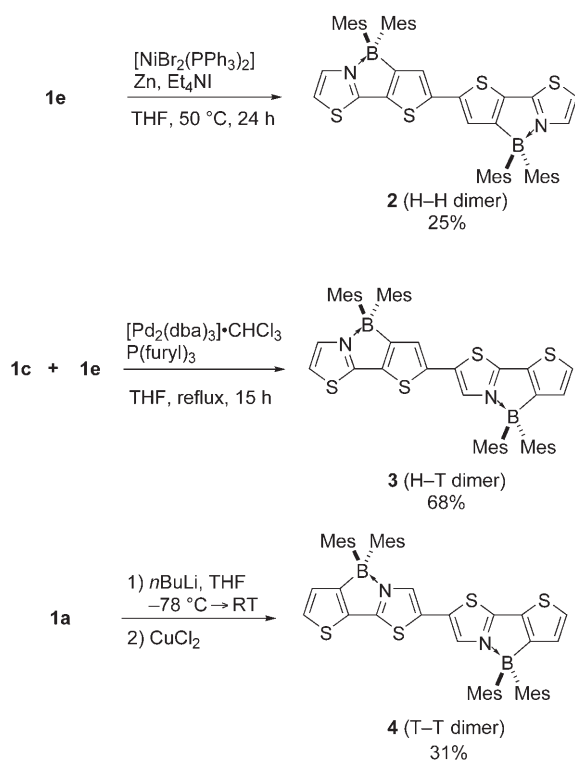
Scheme 2. Synthesis of head-to-head (H–H), head-to-tail (H–T), and tail-to-tail (T–T) dimers **2**–**4**.

denoted as the head and thiazole as the tail. Thus, while the nickel-catalyzed homocoupling of **1e** gave the H–H dimer **2** in 25% yield,[16] the palladium-catalyzed cross-coupling of **1c** and **1e** afforded the H–T dimer **3** in 68% yield.[17] The T–T dimer **4** was obtained in 31% yield by the CuCl₂-promoted oxidative coupling of the monolithiated derivative **1b**, which was generated in situ from **1a**.[18]

The photophysical and electrochemical data for the monomer **1a** and dimers **2**–**4** are summarized in Table 1, in which the corresponding data for 2-thienyl-2-thiazole (the

Table 1: Photophysical[a] and electrochemical[b] data.

Compound	Absorption		Fluorescence		CV	
	λ_{abs} [nm]	log ε	λ_{em} [nm]	Φ_F	E_{pc} [V][c]	$E_{1/2}$ [V][c]
2-thienyl-2-thiazole	313	4.15	373	0.11[d]	−2.95	
1a	333	4.11	452	0.09[d]	−2.41	−2.30
2 (H–H)	443	4.42	492	0.06[e]	−2.00	−1.94
3 (H–T)	427	4.55	486	0.07[e]	−2.08	−2.00
4 (T–T)	414	4.51	472	0.09[e]	−2.06	−1.99
Alq₃					−2.36[f]	
PBD					−2.40[g]	−2.37[g]

[a] In THF. [b] In THF with Bu₄N⁺PF₆⁻ at a scan rate of 100 mVs⁻¹. [c] Potentials vs. ferrocene/ferrocenium. [d] Determined with quinine sulfate as a standard. [e] Determined with perylene as a standard. [f] Ref. [19a] (determined under conditions similar to those described above). [g] Ref. [19b] (determined in *N*-methylpyrrolidine with Bu₄N⁺BF₄⁻). CV = cyclic voltammetry.

parent molecule of **1a** without the boryl group), tris(8-hydroxyquinoline)aluminum (Alq₃), and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) are included for comparison. While the monomer **1a** displays an absorption band at 333 nm, the dimers **2**–**4** display absorption maximum wavelengths in the range 414–443 nm. The boryl-substituted thienylthiazoles **1a** and **2**–**4** show weak fluorescence emissions in the range 452–492 nm. Electrochemical data were determined by cyclic voltammetry and showed an irreversible reduction wave with a peak potential at E_{pc} = −2.95 V for the parent 2-thienyl-2-thiazole. In contrast, boryl-substituted **1a** exhibited a reversible reduction wave, as evident from the areas and proximity of the anodic and cathodic peaks, at a less negative peak potential (E_{pc} = −2.41 V). This result demonstrates that the formation of the intramolecular B–N coordination not only decreases the reduction potential but also stabilizes the produced radical anion. In addition, the extension of the π conjugation on going from the monomer **1a** to the dimers **2**–**4** also shifts the reduction potential to more positive values by about 0.3–0.4 V (E_{pc}: **2** −2.00 V, **3** −2.08 V, **4** −2.06 V); however, the regiochemistry of the dimer structure does not significantly affect the reduction potential. Notably, the reduction potentials of the dimers **2**–**4** are less negative than those of Alq₃ (E_{pc} = −2.36 V)[19a] and PBD (E_{pc} = −2.40 V),[19b] which is indicative of the possible application of **2**–**4** as electron-transporting materials.

We conducted density functional theory (DFT) calculations (B3LYP/6-31G(d) level) on the H–H dimer **2** and its parent analogue, the thienylthiazole dimer **5**. Boryl-substituted **2** has a lower-lying LUMO (by 0.33 eV) than that of **5**. Notably, while both of these compounds have a similar LUMO shape over the entire π-conjugated framework, a difference is observed in their electrostatic-potential maps (Figure 2). In the skeleton of **2**, the thiazole moiety is clearly electronically more positive than the thiophene moiety, thus demonstrating that the B–N coordination enhances the electron-accepting nature of the thiazole ring.

X-ray crystallographic analyses on **2**–**4** revealed that all the dimers have highly π-conjugated coplanar frameworks, each with a dihedral angle of 0° between the monomer units, thus indicative of effective π conjugation extended through
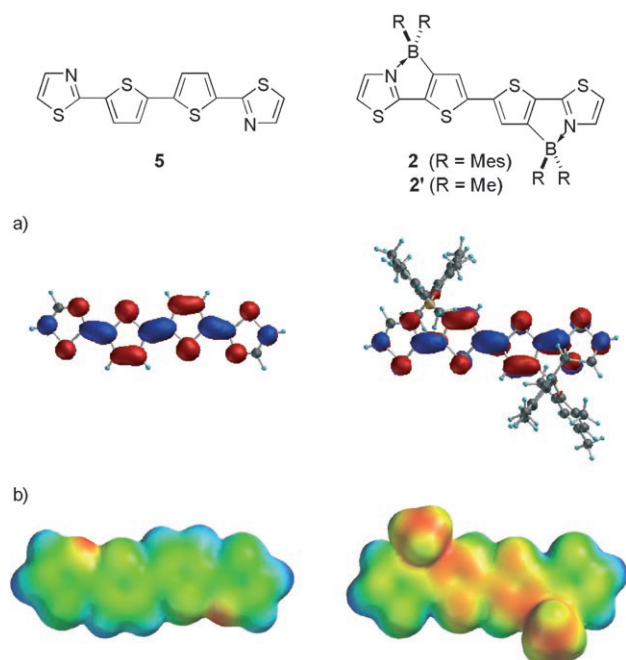
Figure 2. Comparison of electronic structure between **2** and its parent analogue **5**: a) Pictographic drawings of LUMOs and b) electrostatic-potential maps, in which a dimethylboryl analogue **2'** is employed as a model of **2**, clearly show the difference in the electrostatic nature between the thiazole and thiophene rings in **2'**.

Figure 3. a) Structural formula and perspective view of the crystal packing in **2** and b) side view of the one-dimensional π stacking in **2**. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbon atom from each mesityl group is shown in (b).

the dimer skeletons. The H–H dimer **2** forms an interesting π-stacking structure (Figure 3).[15] In this structure, the molecules are arranged in an offset face-to-face π-stacking array with an interplanar distance of 3.60 Å, such that the thiophene moiety and the thiazole moiety are facing each other (Figure 3a). The intermolecular electrostatic interaction might be partly responsible for the formation of this packing structure since the thiophene and the thiazole moieties in the skeleton of **2** can be regarded as electron-donating and electron-accepting moieties, respectively. In conjunction with this solid-state structure, it is noteworthy that **2** has a relatively high electron mobility of $\mu = 1.5 \times 10^{-4}$ cm^{2}V^{-1}s^{-1},[20] while this compound did not show any hole-transporting ability, according to a preliminary time-of-flight (TOF) carrier-mobility measurement on its vacuum-deposited film.

In summary, the boryl-substituted thienylthiazole **1a** was designed and synthesized as a new building unit for electron-transporting materials. On the basis of the regioselective functionalization of **1a**, a series of regioisomeric dimers was also prepared. The studies of their structures and properties showed that the intramolecular B–N coordination effectively fixes the π-conjugated framework in a planar fashion and substantially affects the electronic structure through an increase in the electron affinity. These results clearly demonstrate the potential of this molecular design for electron-transporting materials. Importantly, the present concept is simple and general, and should be applicable to other N-heteroaromatic ring-based π-electron systems. Further development of new n-type semiconducting materials along this line is now in progress.
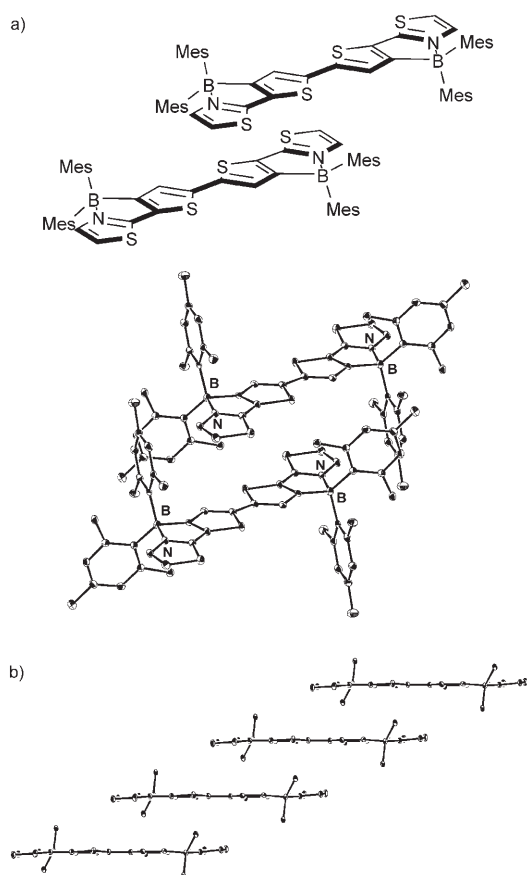
Experimental Section
Full experimental details and analytical data can be found in the Supporting Information.

1a: A solution of *n*BuLi (16.8 mL, 1.60 M in hexane, 26.9 mmol) was added dropwise to a solution of (3-bromo-2-thienyl)-2-thiazole (6.61 g, 26.9 mmol) in diethyl ether (150 mL) at −78 °C. After the mixture was stirred at −78 °C for 1.5 h, a solution of dimesitylfluoroborane (7.27 g, 26.9 mmol) in diethyl ether (50 mL) was added to the mixture by cannula. The reaction mixture was gradually warmed to room temperature and stirred for 4 h. The solvent was removed under reduced pressure, and the mixture was purified by silica gel column chromatography (CH$_2$Cl$_2$, $R_f = 0.53$). Recrystallization from a mixed solvent of CH$_2$Cl$_2$/hexane gave 8.36 g (20.1 mmol) of **1a** as pale yellow crystals in 75% yield. M.p. 233–235 °C; ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 7.69$ (d, $J_{HH} = 5.2$ Hz, 1 H), 7.46 (d, $J_{HH} = 6.8$ Hz, 1 H), 7.25 (d, $J_{HH} = 6.8$ Hz, 1 H), 6.99 (d, $J_{HH} = 5.2$ Hz, 1 H), 6.67 (s, 4 H), 2.21 (s, 6 H), 1.88 ppm (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 166.6$, 139.9, 137.2, 134.0, 133.3, 130.7, 129.4, 129.1, 116.3, 24.3, 20.8 ppm (two peaks for the boron-bound carbon atoms are not observed as a result of quadrupolar relaxation); ^{11}B NMR (128 MHz, CDCl$_3$): $\delta = 3.52$ ppm; EI-MS: m/z: 415 [M^+]. Elemental analysis calcd (%) for C$_{25}$H$_{26}$BNS$_2$: C 72.28, H 6.31, N 3.37; found: C 72.26, H 6.25, N 3.28.

[1] For recent reviews, see: a) G. Hughes, M. R. Bryce, *J. Mater. Chem.* **2005**, *15*, 94; b) A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4556; c) C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J.-L. Brédas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, *16*, 4436; d) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99.

[2] a) C. Adachi, T. Tsutsui, S. Saito, *Appl. Phys. Lett.* **1989**, *55*, 1489; b) M. Meier, E. Buchwald, S. Karg, P. Pösch, M. Greczmiel, P. Strohriegl, W. Rieß, *Synth. Met.* **1996**, *76*, 95; c) J. Bettenhausen, P. Strohriegl, *Adv. Mater.* **1996**, *8*, 507; d) N. Tamoto, C. Adachi, K. Nagai, *Chem. Mater.* **1997**, *9*, 1077; e) Z. Peng, Z. Bao, M. E. Galvin, *Adv. Mater.* **1998**, *10*, 680; f) H.-C. Yeh, R.-H. Lee, L.-H. Chan, T.-Y. J. Lin, C.-T. Chen, E. Balasubramaniam, Y.-T. Tao, *Chem. Mater.* **2001**, *13*, 2788; g) C. Wang, G.-Y. Jung, Y. Hua, C. Pearson, M. R. Bryce, M. C. Petty, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, *Chem. Mater.* **2001**, *13*, 1167.

[3] a) J. Kido, C. Ohtaki, K. Hongawa, K. Okuyama, K. Nagai, *Jpn. J. Appl. Phys.* **1993**, *32*, L917; b) M. Strukelj, F. Papadimitrakopoulos, T. M. Miller, L. J. Rothberg, *Science*, **1995**, *267*, 1969; c) M. Strukelj, T. M. Miller, F. Papadimitrakopoulos, S. Son, *J. Am. Chem. Soc.* **1995**, *117*, 11976.

[4] a) S. E. Tunney, J. Suenaga, J. K. Stille, *Macromolecules* **1983**, *16*, 1398; b) T. Kanbara, N. Saito, T. Yamamoto, K. Kubota, *Macromolecules* **1991**, *24*, 5883; c) T. Kanbara, T. Yamamoto, *Macromolecules* **1993**, *26*, 3464; d) J. Bettenhausen, M. Greczmiel, M. Jandke, P. Strohriegl, *Synth. Met.* **1997**, *91*, 223; e) M. Jandke, P. Strohriegl, S. Berleb, E. Werner, W. Brütting, *Macromolecules* **1998**, *31*, 6434; f) C. J. Tonzola, M. M. Alam, S. A. Jenekhe, *Adv. Mater.* **2002**, *14*, 1086; g) Y. Zhu, M. M. Alam, S. A. Jenekhe, *Macromolecules* **2003**, *36*, 8958.

[5] a) T. Yamamoto, T. Maruyama, Z. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, K. Kuboda, *J. Am. Chem. Soc.* **1994**, *116*, 4832; b) C. Wang, M. Kilitziraki, J. A. H. MacBride, M. R. Bryce, L. E. Horsburgh, A. K. Sheridan, A. P. Monkman, I. D. W. Samuel, *Adv. Mater.* **2000**, *12*, 217.

[6] J. A. Osaheni, S. A. Jenekhe, *Chem. Mater.* **1992**, *4*, 1282.

[7] T. Kanbara, T. Yamamoto, *Chem. Lett.* **1993**, 419.

[8] a) Y. Saitoh, T. Yamamoto, *Chem. Lett.* **1995**, 785; b) S. Naka, H. Okada, H. Onnagawa, T. Tsutsui, *Appl. Phys. Lett.* **2000**, *76*, 197.

[9] a) R. Fink, C. Frenz, M. Thelakkat, H.-W. Schmidt, *Macromolecules* **1997**, *30*, 8177; b) R. Fink, Y. Heischkel, M. Thelakkat, H.-W. Schmidt, C. Jonda, M. Hüppauff, *Chem. Mater.* **1998**, *10*, 3620.

[10] C. J. Tonzola, M. M. Alam, W. Kaminsky, S. A. Jenekhe, *J. Am. Chem. Soc.* **2003**, *125*, 13548.

[11] a) K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974; b) M. Uchida, T. Izumizawa, T. Nakano, S. Yamaguchi, K. Tamao, K. Furukawa, *Chem. Mater.* **2001**, *13*, 2680.

[12] For recent reviews of organoboron materials, see: a) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574; b) C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927.

[13] For planarization using intramolecular hydrogen bonding, see: A. P. Monkman, L.-O. Pålsson, R. W. T. Higgins, C. Wang, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, *J. Am. Chem. Soc.* **2002**, *124*, 6049.

[14] For thienylthiazole-based π-electron systems, see, for example: a) I. H. Jenkins, P. G. Pickup, *Macromolecules* **1993**, *26*, 4450; b) U. Mitschke, E. M. Osteritz, T. Debaerdemaeker, M. Sokolowski, P. Bäuerle, *Chem. Eur. J.* **1998**, *4*, 2211; c) U. Mitschke, T. Debaerdemaeker, P. Bäuerle, *Eur. J. Org. Chem.* **2000**, 425;
d) X. M. Hong, H. E. Katz, A. J. Lovinger, B.-C. Wang, K. Raghavachari, *Chem. Mater.* **2001**, *13*, 4686; e) M.-K. Ng, L. Yu, *Angew. Chem.* **2002**, *114*, 3750; *Angew. Chem. Int. Ed.* **2002**, *41*, 3598; f) M.-K. Ng, D.-C. Lee, L. Yu, *J. Am. Chem. Soc.* **2002**, *124*, 11862; g) J. Cao, J. W. Kampf, M. D. Curtis, *Chem. Mater.* **2003**, *15*, 404; h) J. Cao, M. D. Curtis, *Chem. Mater.* **2003**, *15*, 4424; i) T. Yamamoto, M. Arai, H. Kokubo, S. Sasaki, *Macromolecules* **2003**, *36*, 7986; j) P. Jiang, G. M. Morales, W. You, L. Yu, *Angew. Chem.* **2004**, *116*, 4571; *Angew. Chem. Int. Ed.* **2004**, *43*, 4471; k) M. D. Curtis, J. Cao, J. W. Kampf, *J. Am. Chem. Soc.* **2004**, *126*, 4318; l) J. Lee, B.-J. Jung, S. K. Lee, J.-I. Lee, H.-J. Cho, H.-K. Shim, *J. Polym. Sci. Part A* **2005**, *43*, 1845; m) S. Ando, R. Murakami, J. Nishida, H. Tada, Y. Inoue, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2005**, *127*, 14996.

[15] Crystal data for **1a**: $C_{25}H_{26}BNS_2$, $M_r = 415.40$, crystal dimensions $0.20 \times 0.20 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$, $a = 8.1921(18)$, $b = 10.118(2)$, $c = 13.205(3)$ Å, $\alpha = 90.093(5)$, $\beta = 91.356(5)$, $\gamma = 90.159(5)°$, $V = 1094.3(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.261$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71070$ Å, $T = 173(2)$ K, $2\theta_{max} = 50.0°$, 7314 measured reflections, 3775 independent reflections ($R_{int} = 0.0199$), $R_1 = 0.0406$, w$R_2 = 0.1026$ ($I > 2\sigma(I)$), GOF = 1.043. Crystal data for **2**: $C_{50}H_{50}B_2N_2S_4$, $M_r = 828.78$, crystal dimensions $0.20 \times 0.10 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$, $a = 7.8642(15)$, $b = 15.824(3)$, $c = 17.361(3)$ Å, $\beta = 100.0793(9)°$, $V = 2127.2(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.294$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71070$ Å, $T = 100(2)$ K, $2\theta_{max} = 50.0°$, 14103 measured reflections, 3715 independent reflections ($R_{int} = 0.0333$), $R_1 = 0.0412$, w$R_2 = 0.0956$ ($I > 2\sigma(I)$), GOF = 1.073. Crystal data for **4**: see the Supporting Information. CCDC-292025 (**1a**), CCDC-292026 (**2**), and CCDC-292027 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] M. Iyoda, H. Otsuka, K. Sato, N. Nisato, M. Oda, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80.

[17] V. Farina, B. Krishnan, *J. Am. Chem. Soc.* **1991**, *113*, 9585.

[18] a) T. Kauffmann, *Angew. Chem.* **1974**, *86*, 321; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 291; b) J. Kagan, K. Arora, *Heterocycles* **1983**, *20*, 1937.

[19] a) Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, S. Tokito, Y. Taga, *J. Am. Chem. Soc.* **2000**, *122*, 1832; b) S. Janietz, A. Wedel, *Adv. Mater.* **1997**, *9*, 403.

[20] For comparison, reported electron mobilities for the representative materials by means of TOF measurements: Alq$_3$ ($\mu = \approx 1 \times 10^{-5}$ cm^2 V^{-1} s^{-1}),[20a] PBD ($\mu = 1.9 \times 10^{-5}$ cm^2 V^{-1} s^{-1}),[20b] silole derivatives ($\mu \approx 2 \times 10^{-4}$ cm^2 V^{-1} s^{-1}),[20c] 1,10-phenanthroline ($\mu = 5.2 \times 10^{-4}$ cm^2 V^{-1} s^{-1}),[8b] and ter(9,9-diarylfluorene)s ($\mu \approx 1.2 \times 10^{-3}$ cm^2 V^{-1} s^{-1});[20d] see: a) S. Barth, P. Müller, H. Riel, P. F. Seidler, W. Rieß, H. Vestweber, H. Bässler, *J. Appl. Phys.* **2001**, *89*, 3711; b) T. Yasuda, Y. Yamaguchi, D.-C. Zou, T. Tsutsui, *Jpn. J. Appl. Phys.* **2002**, *41*, 5626; c) H. Murata, G. G. Malliaras, M. Uchida, Y. Shen, Z. H. Kafafi, *Chem. Phys. Lett.* **2001**, *339*, 161; d) C.-C. Wu, T.-L. Liu, W.-Y. Hung, Y.-T. Lin, K.-T. Wong, R.-T. Chen, Y.-M. Chen, Y.-Y. Chien, *J. Am. Chem. Soc.* **2003**, *125*, 3710.