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# Synthesis, Properties, and Structures of Benzo[1,2-*b*:4,5-*b*′]bis[*b*]benzothiophene and Benzo[1,2-*b*:4,5-*b*′]bis[*b*]benzoselenophene

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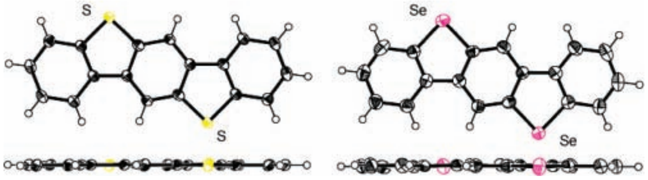
## ABSTRACT



**Employing two consecutive cyclization reactions, benzo[1,2-*b*:4,5-*b*′]bis[*b*]benzochalcogenophenes, which are $\pi$-extended heteroarenes, were efficiently synthesized. Their electronic and crystal structures were elucidated on the basis of UV–vis spectra, electrochemical measurements, and X-ray structural analyses.**

The synthesis and characterization of $\pi$-extended heteroarenes containing chalcogenophenes (i.e., thiophene and/or selenophene) in fused aromatic ring systems are of current interest owing to their potential applications as organic semiconductors for various optoelectronic devices, such as organic field-effect transistors (OFETs), light emitting diodes (LEDs), and photovoltaic cells.[1] In particular, their use in OFETs has been actively investigated owing to their structural resemblance to oligoacenes, such as pentacene, one of the best organic semiconductors for OFET devices that show very high-field-effect mobility ($\sim$3.0 cm$^2$ V$^{-1}$ s$^{-1}$).[2] New $\pi$-extended heteroarenes, e.g., thieno[*n*]acenes,[3] thiophene−benzene annulated acene-like compounds,[1a,4] and thiophene-containing *peri*-fused aromatics,[5] have been developed and tested as active semiconducting channels in OFET devices.

From the viewpoint of synthetic chemistry, however, efficient synthetic strategies for highly extended analogues possessing more than four aromatic rings are limited.[6] In this context, the Bergman cycloaromatization, which involves

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(1) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028−5048. (b) See also a special issue on organic electronics: *Chem. Mater.* **2004**, *16*, 4381−4846.

(2) (a) Lin, Y. Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606−608. (b) Kelly, T. W.; Boardman, L. D.; Dunbar, T. D.; Muyres, D. V.; Pellerite, M. J.; Smith, T. P. *J. Phys. Chem. B* **2003**, *107*, 5877−5881.

(3) (a) Li, X.-C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206−2207. (b) 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*, 13281−13286.

(4) (a) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *8*, 36−39. (b) Sirringhaus, H.; Friend, R. H.; Wang, C.; Leuninger, J.; Mullen, K. *J. Mater. Chem.* **1999**, *9*, 2095−2101. (c) Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5084−5085. (d) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986−4987. (e) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604−12605. (f) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044−3050. (g) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224−2226.

(5) Takimiya, K.; Kunugi, Y.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2005**, *127*, 3605−3612.

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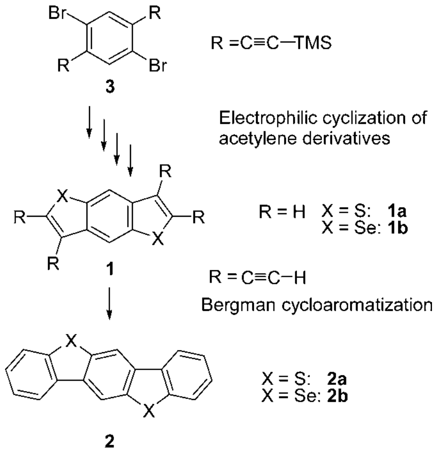
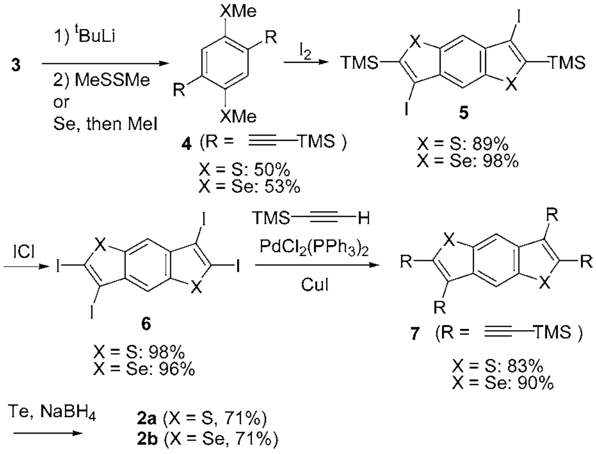
the conversion of *o*-bis(ethynyl)benzene into naphthalene, is one of the potential reactions for the synthesis of $\pi$-extended aromatic compounds.[7] Although to our best knowledge only a few examples of the Bergman cycloaromatization on chalcogenophenes have been reported,[8] we thought that the reaction was worth considering in the synthesis of highly extended heteroarenes and planned to examine the Bergman double cyclization on benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes (**1**, Scheme 1),[9] which gives benzo[1,2-*b*:4,5-*b*′]bis[*b*]benzochalcogenophenes (**2**)[10] possessing five aromatic rings fused in a linear fashion. In this approach, the tetraethynyl derivative of **1** is a rational precursor. Since various derivatives of **1** are readily synthesized by double electrophilic heterocyclization of the central benzene core,[9] the combination of these two cyclization protocols can provide a unique and efficient synthetic approach to **2** (five aromatic rings) from a benzene derivative (one aromatic ring) via **1** (three aromatic rings). We here report the efficient synthesis of **2** by this approach, their properties and crystal structures, and the preliminary results of FET characteristics of their evaporated thin films.

**Scheme 1.** Consecutive Double Cyclization Approach to **2**



Scheme 2 shows the synthetic route to **2**. Readily available 1,4-dibromo-2,5-bis(trimethylsilylethynyl)benzene (**3**)[11] was converted into 1,4-bis(methylthio)- or 1,4-bis(methylseleno)-2,5-bis(trimethylsilylethynyl)benzene (**4**), which was utilized in the Larock protocol to form benzo[1,2-*b*:4,5-*b*′]dichalcogenophene derivatives (**5**).[12] The trimethylsilyl groups on **5** were substituted with iodine to give tetraiodo compounds (**6**), and these were readily converted into tetrakis(trimethylsilylethynyl) derivatives (**7**) by the Sonogashira coupling reaction. Formation of the outermost benzene rings of **2** was achieved in reasonable yields with the Bergman cycloaromatization, using in situ generated sodium telluride as reagent.[13] Under the reaction conditions of the final step, desilylation was concomitantly induced to give **2** directly. Both sulfur (**2a**) and selenium (**2b**) analogues were stable pale yellow solids that were well-characterized by spectroscopic and combustion elemental analyses. Single-crystal X-ray analyses enabled unquestionable characterization of these highly extended heterocycles (vide infra).

**Scheme 2.** Syntheses of **2a** and **2b**



Cyclic voltammetry of **2** showed irreversible oxidation waves (for charts, see Figure S1 in the Supporting Information). The oxidation peaks of **2a** and **2b** were found at +1.15 and +0.89 V (vs Fc/Fc$^+$). The potential of **2a** was much higher than that of **1a** (+0.95 V), whereas the potential of **2b** was comparable to that of **1b** (+0.89 V). On the premise that the Fc/Fc$^+$ energy level is 4.8 eV below the vacuum level,[14] HOMO levels of **2a** and **2b** were estimated by using oxidation onsets (+0.96 V for **2a** and +0.76 V for **2b**) 5.8 and 5.6 eV below the vacuum level, respectively. These values are consistent with the HOMO levels that were calculated by using DFT methods (5.57 eV for **2a** and 5.41 eV for **2b**). It should be noted that the HOMO levels of **2** were similar to or slightly lower than those of **1**, even though the former have a more extended $\pi$-system than the latter, indicating that the electronic structures of **2** are different from those of **1**.

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(6) (a) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2005**, *7*, 5301−5304. (b) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Chem.−Eur. J.* **2007**, *13*, 548−556.

(7) (a) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25−53. (b) For an excellent review, see: Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453−53. (c) Bowles, D. M.; Anthony, J. E. *Org. Lett.* **2000**, *2*, 85−87.

(8) Lo, C.-Y.; Kumar, M. P.; Chang, H.-K.; Lush, S.-F.; Liu, R.-S. *J. Org. Chem.* **2005**, *70*, 10482−10487.

(9) Takimiya, K.; Konda, Y.; Ebata, H.; Niihara, N.; Otsubo, T. *J. Org. Chem.* **2005**, *70*, 10569−10571.

(10) The synthesis of **2a** with conventional synthetic strategies has been reported: (a) Ahmed, M.; Ashby, J.; Ayad, M.; Meth-Cohn, O. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1099−1102. (b) Rao, D. S.; Tilak, B. D. *J. Sci. Ind. Res.* **1958**, *17B*, 260−266. (c) Pandya, L. J.; Pillai, G. N.; Tilak, B. D. *J. Sci. Ind. Res.* **1959**, *18B*, 198−202.

(11) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578−4593.

(12) (a) Yue, D.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 1905−1909. (b) Kesharwani, T.; Worlikar, S. A.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 2307−2312.

(13) (a) Tsuchiya, T.; Sashida, H.; Kurahashi, H. *J. Chem. Soc., Chem. Commun.* **1991**, 802. (b) Landis, C. A.; Payne, M. M.; Eaton, D. L.; Anthony, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1338−1339.

(14) (a) Brédas, J.-L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555−6559. (b) Pommerehne, J.; Vestweber, H.; Guss, W.; Mark, R. F.; Bässler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551−554.

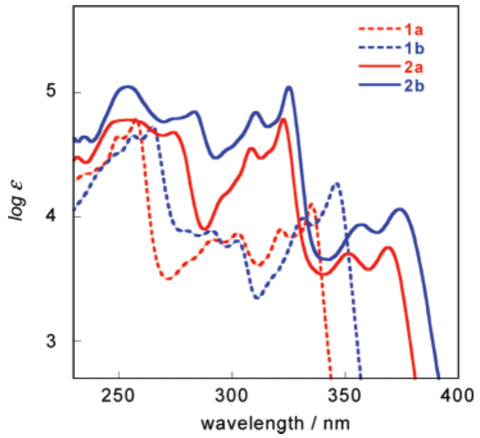

**Figure 1.** UV−vis spectra of **1** and **2** in dichloromethane.

The UV−vis spectra of **2** and **1** are shown in Figure 1 for comparison. **2a** and **2b** have similar absorption bands, indicating no pronounced perturbation by the substitution of chalcogen atoms, although the absorption bands of **2b** are slightly red-shifted. Energy gaps estimated from absorption edges are 3.3 and 3.2 eV for **2a** and **2b**, respectively, which are smaller than those for **1a** (3.6 eV) and **1b** (3.5 eV). The expected LUMO levels of **2a** and **2b** based on oxidation potentials and absorption edges in the UV−vis spectra are 2.5 and 2.4 eV below the vacuum level, respectively, and are lower than those of **1** (2.0 eV). MO calculations using DFT methods reproduced these experimentally estimated energy levels of frontier molecular orbitals (see the Supporting Information). From these results, we can conclude that the fusion of two benzene rings at the periphery of **1** is not simply $\pi$-extension in terms of the electronic structure of the frontier molecular orbitals: the HOMO levels of **2** are comparable to those of **1**, whereas the LUMO levels of **2** are lower (Table 1).

**Table 1.** Electrochemical and UV−Vis Data of **1** and **2** Together with Estimated HOMO and LUMO Levels

| | $E_{\mathrm{ox}}$/V[a] anodic/onset | $\lambda_{\mathrm{max}}$[b]/nm peak/edge | HOMO[c]/eV | Eg[d]/eV | LUMO/eV |
|---|---|---|---|---|---|
| **2a** | +1.15/+0.96 | 369/380 | −5.8 | 3.3 | −2.5 |
| **2b** | +0.89/+0.76 | 374/390 | −5.6 | 3.2 | −2.4 |
| **1a**[e] | +0.95/+0.80 | 335/344 | −5.6 | 3.6 | −2.0 |
| **1b**[e] | +0.89/+0.73 | 350/357 | −5.5 | 3.5 | −2.0 |

[a] Versus Fc/Fc$^+$. [b] Absorption spectra. [c] Estimated from the onset of the oxidation peak. [d] Determined from the absorption edge. [e] Reference 9.

Single-crystal X-ray analyses revealed the exact molecular structures of **2a** and **2b**,[15] where the $\pi$-extended frameworks are almost planar and the maximum deviation from the mean plane is ca. 0.03 Å for **2a** and ca. 0.05 Å for **2b** (Figure S4, Supporting Information). The molecular structures of **2a** and **2b** are the same except for slight differences in C−S and C−Se bond lengths. However, the crystal structures of these two compounds are quite different (Figure 2). The crystal structure of **2a** is based on $\pi$-stacking along the *b*-axis direction in which the plane-to-plane distance is ca. 3.52 Å. The lack of contact between the $\pi$-stacks indicates the one-dimensional (1D) electronic structure of the crystal. In contrast, **2b** assumes the so-called sandwiched herringbone structure in which its dimers are packed tightly in the crystal. The plane-to-plane distance in the dimer is ca. 3.47 Å, and short CH−$\pi$ and C−Se contacts exist in a face-to-edge manner between the dimers, indicative of the two-dimensional electronic structure of the crystal.

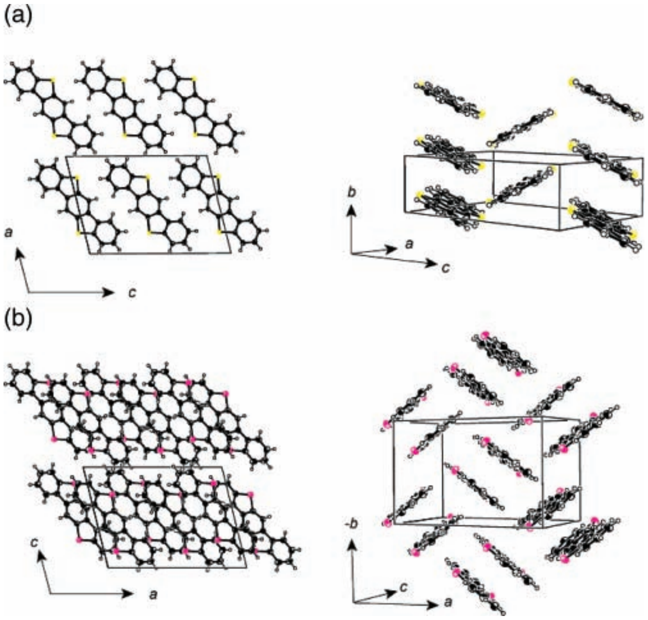

**Figure 2.** Crystal structures of **2a** (a) and **2b** (b).

Preliminary studies on FET devices made of **2** were carried out. Physical vapor deposition of **2** gave homogeneous thin films with a metallic luster on the Si/SiO$_2$ substrate that was modified with octyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS),[16] although no film was deposited when the substrate temperature exceeded 40 °C. Considering the fact that small heteroaromatic systems, such as **1** (three aromatic rings) and [1]benzochalcogenopheno[3,2-*b*][1]-benzochalcogenophene (four aromatic rings, Figure 3), did not afford homogeneous thin films by vapor deposition, extension of the $\pi$-conjugated system in heteroarenes is beneficial for practical application to thin-film-based organic devices.

On top of the evaporated thin films gold source and drain electrodes were deposited through a shadow mask to complete the fabrication of "top-contact" devices with *W*/*L*

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(15) See the Supporting Information for details.

(16) Thin film XRDs are available: see the Supporting Information.

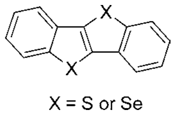

**Figure 3.** Structure of [1]benzochalcogenopheno[3,2-*b*][1]benzochalcogenophenes.

= ca. 30. Field-effect mobilities ($\mu_{\mathrm{FET}}$) evaluated from the saturation regime were of the order of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ (Table 2 and Figure 4). These inferior FET characteristics can be related to the molecular arrangements in the solid state: 1D $\pi$-stacking (**2a**) or the sandwiched herringbone structure (**2b**) may not be suitable for high-performance OFET devices.

**Table 2.** FET Characteristics of Devices Fabricated on Si/SiO$_2$ Substrates with Different Surface Treatments

| material | surfactant | $\mu_{\mathrm{FET}}{}^{a}$/ cm$^2$ V$^{-1}$ s$^{-1}$ | $I_{\mathrm{on}}/I_{\mathrm{off}}$ |
|---|---|---|---|
| **2a** | OTS | $2.4 \times 10^{-3}$ | $10^5$ |
| | HMDS | $2.1 \times 10^{-3}$ | $10^6$ |
| **2b** | OTS | $3.0 \times 10^{-3}$ | $5 \times 10^5$ |
| | HMDS | $3.8 \times 10^{-3}$ | $5 \times 10^7$ |

[a] Estimated from the saturation regime.

In summary, we have established an efficient method to synthesize highly $\pi$-extended heteroarenes, **2a** and **2b**, using two cyclization protocols. Detailed studies of the physicochemical properties of the heterocycles revealed that the perturbation effect of fused benzene rings on the electronic structure is not simple: HOMO levels of **2** are almost the same as or slightly lower than those of **1**, whereas LUMO levels are markedly low, resulting in small HOMO−LUMO gaps. As the control of the HOMO level is regarded to be a key factor for the stabilization of p-channel organic semiconductors in FET applications,[17] the present results are informative for the design of stable p-channel organic semiconductors based on new heteroaromatic systems.

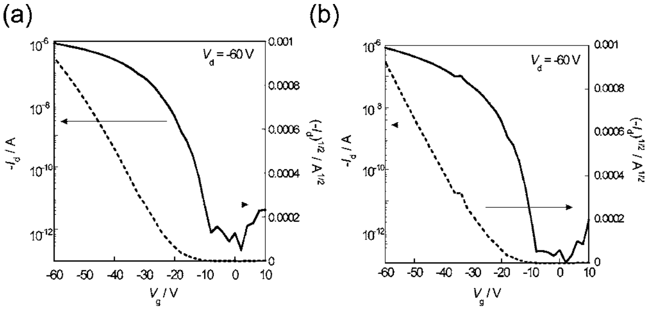

**Figure 4.** Transfer characteristics of **2**-based FETs fabricated on HMDS-treated Si/SiO$_2$ substrate: (a) **2a** and (b) **2b**.

Preliminary results of thin-film deposition and evaluation of FET devices of **2a** and **2b** indicated that these heterocycles with five aromatic rings can form homogeneous thin films by vapor deposition. The obtained thin films act as semiconducting channels, although the field-effect mobilties are low. Further experiments to optimize device fabrication and to elucidate the relationship between structure and properties, particularly molecular arrangement in the thin-film state, as well as FET characteristics, are underway.

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**Supporting Information Available:** Experimental details for the synthesis and characterization of **2a** and **2b**, Crystallographic Information Files (CIFs) for **2a** and **2b**, device fabrication, DFT calculations, and FET characteristics of devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Meng, H.; Bao, Z.; Lovimger, A. J.; Wang, B.-C.; Mujsce, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 9214−9215.