JOC Note

Facile Synthesis, Structure, and Properties of Benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes

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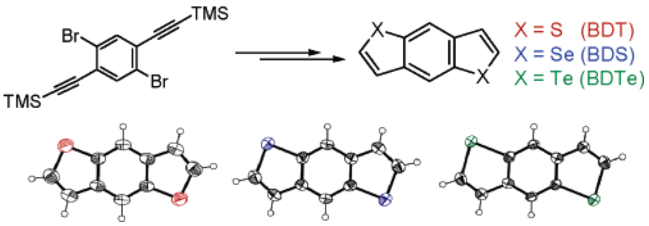
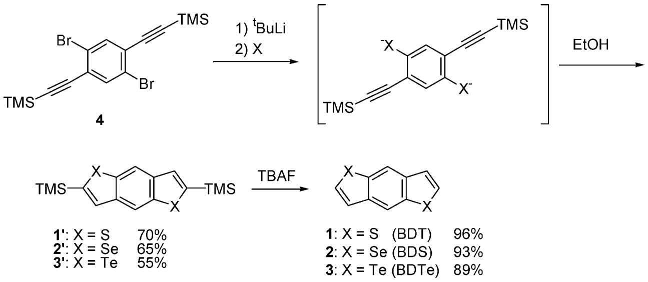
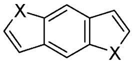


A general and convenient synthesis of benzo[1,2-*b*:4,5-*b*′]-dichalcogenophenes including the thiophene (BDT, **1**), selenophene (BDS, **2**), and tellurophene (BDTe, **3**) homologues is developed. Thus synthesized heterocycles are structurally characterized by single-crystal X-ray analysis, and all three homologues are isostructural with one another. They all have completely planar molecular structures packed in a herringbone arrangement. Their physicochemical properties were also elucidated by means of cyclic voltammetry (CV) and UV−vis spectra.

Thiophene-containing fused-aromatic compounds represent an interesting class of electronic materials utilized for organic conductors,[1,2] narrow band gap polymers,[3,4] and field-effect transistors.[5] Benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT, **1**) is one of such prototypical π-frameworks and has been widely used.[5a,6] The selenium and tellurium homologues, benzo[1,2-*b*:4,5-*b*′]diselenophene (**2**) and benzo[1,2-*b*:4,5-*b*′]diselenophene (**3**), are so far unknown,[7] but these heterocycles are very intriguing in view of development of new electronic materials, because in general, carrier transport in organic solids is governed by intermolecular overlap, which can be enhanced by intermolecular chalcogen-chalcogen contacts. In this regard, it is important to develop an effective synthetic method for these heterocycles as a key molecular framework for novel functional materials. We report here a general synthetic route to the parent benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes (**1**−**3**), the X-ray structures, and electrochemical and photochemical properties of the materials.

SCHEME 1. Synthesis of Benzodichalcogenophenes 1−3





1: X = S (BDT)
2: X = Se (BDS)
3: X = Te (BDTe)

Synthesis. The reported syntheses of the sulfur compound, BDT (**1**), by Kossmehl et al.[8] or Katz et al.,[5a] require thiophene derivatives as key starting materials. Because of limited availability of selenophene and tellurophene derivatives,[9] we sought a different synthetic strategy applicable to not only **1** but also BDS (**2**) and BDTe (**3**). Thus, starting from the central benzene part we examined an intramolecular cyclization reaction between the acetylene substituents and the chalcogenate anion intermediates (Scheme 1).[10]

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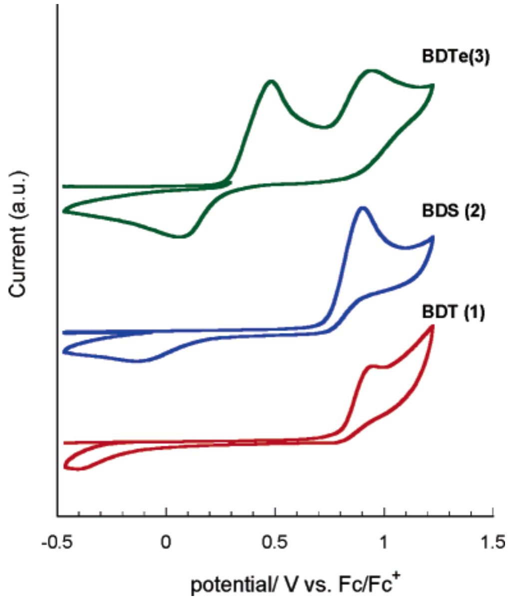

FIGURE 1. Cyclic voltammograms of **1**−**3**.

TABLE 1. Electrochemical and UV−vis Data of 1−3 Together with Their Estimated HOMO and LUMO Levels

	$E_{ox}{}^{a}$ (V) anodic/onset	$\lambda_{max}{}^{b}$ (nm) peak/edge	HOMO^{c} (eV)	$E_g{}^{d}$ (eV)	LUMO (eV)
BDT (**1**)	+0.95/+0.80	335/344	−5.6	3.6	−2.0
BDS (**2**)	+0.89/+0.73	350/357	−5.5	3.5	−2.0
BDTe (**3**)	+0.48/+0.29	380/398	−5.1	3.1	−2.0

^{a} Versus Fc/Fc^{+}. ^{b} Absorption spectra. ^{c} Estimated from the onset of oxidation peak. ^{d} Determined from absorption edge.

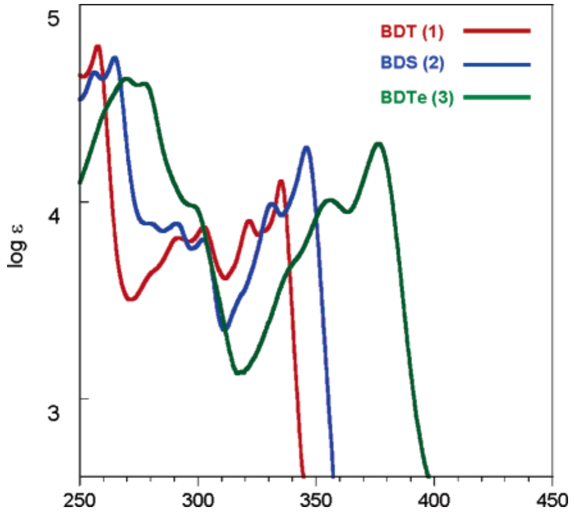

FIGURE 2. UV−vis spectra of **1**−**3** in THF.

For the synthesis of **1**, 1,4-dibromo-2,5-bis(2-trimethylsilylethynyl)benzene (**4**) prepared from 1,4-dibromo-2,5-diiodobenzene and trimethylsilylacetylene by the palladium-catalyzed Sonogashira coupling[11] was treated consequently with ^{t}BuLi and elemental sulfur, and the reaction was finally quenched by addition of alcohol. After the usual workup and purification by column chromatography, desired 2,6-bis(trimethylsilyl)benzo[1,2-*b*:4,5-*b*′]dithiophene (**1′**) was isolated in 70% yield, which was then easily desilylated by a treatment with tetrabutylammonium fluoride (TBAF) to give **1** in 96% yield. In a similar manner, BDS (**2**) and BDTe (**3**) were synthesized using selenium and tellurium powder, respectively, via bis(trimethylsilyl)derivatives **2′** and **3′**, respectively. Two novel heterocycles **2** and **3** were fully characterized by spectroscopic and combustion elemental analyses.

X-ray Structure Analysis. Single crystals of suitable quality for X-ray analysis were obtained by sublimation[12] for BDT (**1**) or recrystallization from chloroform for BDS (**2**) and BDTe (**3**). Compounds **1**−**3** are isostructural to one another with triclinic *P*-1 space group. The unit cells consist of two crystallographically independent molecules, both of which are located at the inversion center. All of these benzodichalcogenophenes are completely planar as shown in Figure S1 and crystallize in a typical herringbone arrangement (see Supporting Information, Figures S1 and S2).

Electrochemical and Photochemical Properties. Electrochemical studies were carried out by means of cyclic voltammetry (CV). All of these heterocycles show irreversible oxidation waves (Figure 1), and the oxidation potentials (Table 1) defined by anodic peaks shift cathodically from +0.95 V (vs Fc/Fc^{+}) for BDT (**1**) to +0.48 V for BDTe (**3**), indicating that the HOMO level elevates in the order of BDT (**1**) < BDS (**2**) ≪ BDTe(**3**). From the onset of the oxidation peaks listed in Table 1, the HOMO levels of these compounds are roughly estimated to be −5.6 eV for **1**, −5.5 eV for **2**, and −5.1 eV for **3** under the premise that the energy level of Fc/Fc^{+} is 4.8 eV below the vacuum level.[13]

UV−vis spectra of the present benzodichalcogenophenes (**1**−**3**) shown in Figure 2 are similar to one another in shape, reflecting their similar electronic structures. They consist of three bands, located at around ~260, 300, and 330−400 nm. The first and the third bands shift bathochromically in the order of BDT (**1**), BDS (**2**), and BDTe (**3**). Since the third band can be assigned as the $\pi-\pi^*$ transition, HOMO−LUMO energy gap is estimated to be 3.1−3.6 eV from the absorption edges. Taking into account the HOMO levels of **1**−**3** determined electrochemically, the LUMO levels of **1**−**3** are estimated to be almost the same (Table 1). This means that the chalcogen atoms in the present π-framework do not play an important role in the LUMO, whereas they do in the HOMO. This consideration is qualitatively supported by MO calculations.[14] The HOMO and LUMO of BDT (**1**) are depicted in Figure 3 as representative of the benzodichalcogenophene system. It should be noted that large coefficients reside on the chalcogen atoms in the HOMO,

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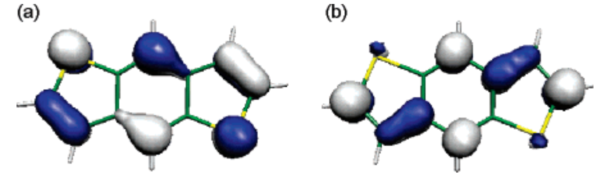

FIGURE 3. Optimized geometry and frontier orbitals of BDT (**1**) at the B3LYP-6-31G(d) level: (a) HOMO and (b) LUMO.

and on the contrary the coefficients on the chalcogen atoms in the LUMO are fairly small.

By employing 1,4-dibromo-2,5-bis(2-trimethylsilylethynyl)benzene (**4**) as a common intermediate, all of the benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes (**1**−**3**) are effectively synthesized via double-heterocycle formation. The resulting heteroarens **1**−**3** have a planar molecular structure and assume a herringbone packing in their crystal structures elucidated by X-ray crystallographic analysis.

Studies on electrochemical properties and UV−vis spectra of the benzodichalcogenophenes gave a rough estimation of the levels of their frontier orbitals. Rather lower oxidation potentials were recorded for the tellurium homologue, BDTe (**3**), which has the highest HOMO level among the three compounds. On the other hand, the LUMO levels estimated from the HOMO−LUMO energy gap determined by the absorption edge in UV−vis spectra are almost the same. These experimental results can be understood by the nature of the calculated frontier molecular orbitals. Thus, benzo[1,2-*b*:4,5-*b*′]chalcogenophenes with heavy chalcogen atoms, especially tellurium atoms, are expected to be a suitable component for the *p*-type (hole transporting) organic semiconductor rather than the *n*-type (electron transporting).

Experimental Section

1,4-Dibromo-2,5-bis(2-trimethylsilylethynyl)benzene (4).[11] Trimethylsilylacetylene (5.8 mL, 41 mmol), $PdCl_2(PPh_3)_2$ (400 mg, 0.6 mmol), and CuI (235 mg, 1.2 mmol) were added successively to a deaerated solution of 1,4-dibromo-2,5-diiodobenzene[11,15] (10.0 g, 21 mmol) in diisopropylamine (60 mL) and benzene (100 mL). The resulting mixture was stirred for 1 h at room temperature, then diluted with water (150 mL), and extracted with ether (60 mL × 2). The extract was washed with water (60 mL × 2) and dried ($MgSO_4$). Evaporation of the solvent gave an oily residue, which was subjected to column chromatography on silica gel eluted with hexane to give 1,4-dibromo-2,5-bis(trimethylsilylethynyl)benzene as a colorless solid (8.4 g, 97%): mp 167−170 °C; ^{1}H NMR δ 0.27 (s, 18H), 7.67 (s, 2H); ^{13}C NMR δ −0.3, 101.4, 103.0, 123.7, 126.4, 136.4; MS (EI) *m/z* 428 (M^+).

Typical Procedure for Synthesis of 2,6-Bis(trimethylsilyl)benzo[1,2-*b*:4,5-*b*′]dichalcogenophens (1′−3′). 2,6-Bis(trimethylsilyl)benzo[1,2-*b*:4,5-*b*′]diselenophene (2′). To a solution of **4** (0.4 g, 1.0 mmol) in ether (15 mL) at −78 °C was added a pentane solution of ^{t}BuLi (1.4 M, 2.9 mL, 4.0 mmol). The resulting mixture was stirred at the same temperature for 15 min and then gradually warmed to room temperature. Selenium powder (0.16 g, 2.0 mmol) was then added in one portion, and the resulting mixture was stirred for 15 min. After addition of ethanol (30 mL), the mixture was further stirred for 1 h and then extracted with chloroform (20 mL × 3). The extract was washed with water (20 mL × 3), dried over $MgSO_4$ (anhydrous), and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluted with hexane ($R_f = 0.4$) to give colorless microcrystals after recrystallization from hexane (0.3 g, 65%): mp 181−184 °C; ^{1}H NMR δ 0.38 (s, 18H), 7.71 (s, 2H), 8.31 (s, 2H); ^{13}C NMR δ −0.1, 121.5, 133.6, 140.8, 141.6, 148.1; MS (EI) *m/z* 430 (M^+). Anal. Calcd for $C_{16}H_{22}Se_2Si_2$: C, 44.85; H, 5.18. Found: C, 44.77; H, 5.03.

2,6-Bis(trimethylsilyl)benzo[1,2-*b*:4,5-*b*′]dithiophene (1′). Compound **1′** was prepared from **4** by a similar reaction as colorless microcrystals (hexane), 70% yield: mp 191−192 °C; ^{1}H NMR δ 0.39 (s, 18H), 7.45 (s, 2H), 8.26 (s, 2H); ^{13}C NMR δ −0.4, 116.0, 129.8, 139.1, 140.7, 143.6; MS (EI) *m/z* 334 (M^+). Anal. Calcd for $C_{16}H_{22}S_2Si_2$: C, 57.42; H, 6.63. Found: C, 57.62; H, 6.83.

2,6-Bis(trimethylsilyl)benzo[1,2-*b*:4,5-*b*′]ditellurophene (3′). Pale yellow plates from chloroform, 55% yield: mp 234−235 °C; ^{1}H NMR δ 0.34 (s, 18H), 8.14 (s, 2H), 8.34 (s, 2H); ^{13}C NMR δ 0.4, 130.7, 131.0, 141.4, 142.7, 147.9; MS (EI) *m/z* 530 (M^+). Anal. Calcd for $C_{16}H_{22}Si_2Te_2$: C, 36.55; H, 4.22. Found: C, 36.30; H, 4.25.

Typical Procedure for the Synthesis of Benzo[1,2-*b*:4,5-*b*′]dichalcogenophens (1−3). Benzo[1,2-*b*:4,5-*b*′]diselenophene (2). To a solution of **2′** (0.23 g, 0.5 mmol) in THF (10 mL) was added a solution of tetrabutylammonium fluoride (1.0 M, 1.1 mL, 1.1 mmol), and the resulting solution was stirred at room temperature for 3 h. Addition of water (20 mL) made a precipitate, which was collected by filtration. The product was successively washed with water (10 mL) and ethanol (10 mL) and dried. Recrystallization from chloroform gave analytical sample of **2** as colorless plates (0.13 g, 93%): mp 255−257 °C (in a sealed tube); ^{1}H NMR δ 7.58 (d, J = 5.9, 2H), 7.98 (d, J = 5.9, 2H), 8.35 (s, 2H); ^{13}C NMR δ 122.0, 126.8, 128.8, 137.8, 139.8; MS (EI) *m/z* 286 (M^+). Anal. Calcd for $C_{10}H_6Se_2$: C, 42.28; H, 2.14. Found: C, 42.27; H, 2.16. UV−vis (in THF): λ_{max} (ϵ) = 256 (45328), 265 (53924), 291 (7746), 302 (6433), 318 (3267), 331 (9763), 346 (18774) nm. PL (in THF): λ_{max} = 367 nm ($\Phi = 2.5 \times 10^{-4}$).

Benzo[1,2-*b*:4,5-*b*′]dithiophene (1)[8]**.** Compound **1** was prepared from **1′** by a similar reaction, 96% yield: mp 199−201 °C (197.5−198.0)[8]; ^{1}H NMR δ 7.35 (d, J = 5.5 Hz, 2H), 7.46 (d, J = 5.5 Hz, 2H), 8.31 (s, 2H); ^{13}C NMR δ 116.8, 122.9, 127.0, 137.1, 137.5; MS (EI) *m/z* 190 (M^+). UV−vis (in THF): λ_{max} (ϵ) = 258 (61848), 280 (4316), 292 (6571), 302 (7432), 322 (7980), 335 (12722) nm; PL (in THF): λ_{max} = 343 nm (Φ = 0.078).

Benzo[1,2-*b*:4,5-*b*′]ditellurophene (3). Yield 89%; mp 283−285 °C (melt with decomposition); ^{1}H NMR δ 7.88 (d, J = 7.1 Hz, 2H), 8.30 (s, 2H), 8.64 (d, J = 7.1 Hz, 2H); ^{13}C NMR δ 120.4, 129.1, 130.9, 135.4, 145.0; MS (EI) *m/z* 386 (M^+). Anal. Calcd for $C_{10}H_6Te_2$: C, 31.49; H, 1.59. Found: C, 31.59; H, 1.39. UV−vis (in THF): λ_{max} (ϵ) = 2709 (42178), 277 (39851), 295 (9899), 339 (4610), 356 (10183), 376 (19740) nm.

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Supporting Information Available: Crystallographic Information Files (CIF) for **1**−**3**, ORTEP drawings of molecular structures of **1**−**3**, crystal structure of **3**, photo luminescence (PL) spectra of **1** and **2**, and details for molecular orbital (MO) calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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