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Graphical Abstract



General synthesis, structure, and optical properties of benzothiophene-fused benzoheteroles containing Group 15 and 16 elements

Mio Matsumura^a, Atsuya Muranaka^{b,*}, Rina Kurihara^c, Misae Kanai^b, Kengo Yoshida^b, Naoki Kakusawa^c, Daisuke Hashizume^d, Masanobu Uchiyama^{b,e}, and Shuji Yasuike^{a,*}

^a School of Pharmaceutical Sciences, Aichi Gakuin University, 1-100 Kusumoto-cho, Chikusa-ku,

Nagoya 464-8650, Japan

Wako 351-0198, Japan

^b Elements Chemistry Laboratory, RIKEN, and Advanced Elements Chemistry Research Team, RIKEN, Center for Sustainable Resource Science (CSRS), Wako, 351-0198, Japan

^c Faculty of Pharmaceutical Sciences, Hokuriku University, Ho-3 Kanagawa-machi, Kanazawa 920-1181, Japan

^d Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science (CEMS),

^e Graduate School of Pharmaceutical Sciences, The University of Tokyo, Tokyo 113-0033, Japan

*Corresponding authors. Tel.: +81 48 467 2857; fax: +81 48 467 2879 (A. M.); tel.: +81 52 757 6775; fax: +81 52 757 6799 (S. Y.); e-mail addresses: atsuya-muranaka@riken.jp (A. Muranaka),

s-yasuik@dpc.agu.ac.jp (S. Yasuike).

ABSTRACT: A series of benzothieno[3,2-*b*]benzoheteroles containing Group 15 (N, P, As, and Sb) and Group 16 (O, S, Se, and Te) elements were synthesized by a versatile method. X-ray analyses revealed that all the tetracyclic heteroacene skeletons were planar. A linear relationship was found between the excitation energies of Group 16-heteroacenes and their atomic radius, in contrast to Group 15-heteroacenes. Density functional theory calculations and electrochemical measurements were performed to understand the structure-optical property relationship.

Keywords

Benzothieno[3,2-b]benzoheterole

Tetracyclic heteroacene

Group 15 and 16 elements

Comprehensive synthesis

Molecular structure

DFT calculation

1. Introduction

Linearly fused heteroacenes are attracting increasing interest owing to their intriguing potential for application in organic semiconductors for organic field-effect transistors (OFETs).¹ Among them, benzothieno [3,2-b] benzothiophene and its derivatives (I) have been widely investigated, leading to the development of high-performance organic semiconductors.^{1c,e,2} In connection with these studies, the benzothiophene-fused benzoheteroles (II), such as nitrogen (M = N-R'),³ phosphorus (M = P-R'),^{3d,4} oxygen (M = O),⁵ and selenium (M = Se)^{1c,e,2c,6} derivatives, have been sporadically prepared to develop synthetic routes and investigate their fundamental, electrochemical, and electronic device properties (Fig. 1). However, to the best of our knowledge, comprehensive synthesis of these heteroacenes has never been carried out. We have been extensively working on the development of novel synthetic methodologies for a library of heterocycles containing Group 15 (N, P, As, and Sb) and Group 16 (O, S, Se, and Te) elements, and have already reported the synthesis and physical properties of 1-benzo[b]heteroles containing a series of Group 15 and 16 elements.⁷ In these articles, replacement of the Group 16 heteroatom leads to a considerable spectral shift, depending on the size of the heteroatom. Here, we report a convergent synthesis of benzothiophene-fused tetracyclic heteroacenes⁸ and a detailed comparison of the molecular structures and optical properties of the obtained heteroacenes. For the Group 15-heteroacenes, 10-phenyl derivatives were targeted because of the stability and handling ability.



Fig. 1. Benzothiophene-fused tetracyclic heteroacenes.

2. Results and discussion

The established convergent synthetic routes to benzothiophene-fused benzoheteroles **3** are shown in Scheme 1. The key precursors **2a** and **2b** were synthesized by I_2 - and Br_2 -mediated electrophilic cyclization of simple diphenyl acetylenes **1a** and **1b**, respectively.⁹ When **1a** was reacted with Br_2 , the desired 2-halophenyl benzofulan derivative was not obtained but the triple bond underwent bromine addition to form a 1,2-dibromoalkene. Compound **2** was treated with *n*- or *t*-BuLi in anhydrous diethyl ether under an argon atmosphere, followed by trapping of the dilithio intermediate with an electrophilic reagent, which resulted in ring closure to afford a range of the desired benzothiophene-fused benzoheteroles (**3b-h**) in moderate yields. Indole derivative **3a** was synthesized by the reaction of **2b** and aniline in the presence of $Pd_2(dba)_3$ and tri-*tert*-butylphosphonium tetrafluoroborate at 125 °C.¹⁰



Scheme 1. Synthesis of benzothiophene-fused benzoheteroles.

For **3a**; method A. aniline (0.5 mmol), **2b** (0.55 mmol), Pd₂(dba)₃ (22 mol%), P(*t*-Bu)₃HBF₄ (22 mol%), *t*-BuONa (1.7 mmol), and toluene (5 mL) at 125 °C. For **3b-d** and **f-h**; method B. **2b** (2.0 mmol), *n*-BuLi (2.4 eq.), Group 15 or 16 reagent (4 mmol), and diethyl ether (40 mL), at -20 °C to rt. For **3e**; method B. **2a** (2.0 mmol), *t*-BuLi (4 eq.), (PhSO₂)₂S (4 mmol), and diethyl ether (30 mL), at -78 °C to rt.

We successfully obtained single crystals of all the heteroacenes and then carried out X-ray analysis.^{2e,11} Selected bond lengths and angles are summarized in the Supporting Information, and the ORTEP drawings are provided in Fig. 2. Fig. 2 clearly shows that the tetracyclic skeletons are planar. As expected, with the increase in the size of the heteroatom, the carbon-heteroatom bond lengths (M-C2 and M-C3) increase, and the C2-M-C3 bond angles decrease. The P, As, and Sb atoms in the Group 15-heteroacenes were tetrahedrally coordinated. This is in contrast to the planar coordination of the N

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atom in **3a**, in which the bond angles are close to 120° [C2-N-C(Ph): $123.6(2)^{\circ}$; C3-N-C(Ph): $128.2(2)^{\circ}$]. The bond lengths and angles in **3b** and **3c** were essentially the same as those in 1-phenylphosphindole and 1-phenylarsindole, except for the C3-C4 bond length. The C3-C4 bond lengths in **3b** (1.3718(14) Å) and **3c** (1.362(3) Å) are considerably longer than the corresponding C-C bond lengths in 1-phenylphosphindole (1.326(4) Å)¹² and 1-phenylarsindole (1.330(3) Å)^{7b}, respectively, which implies that benzothiophene-fusion significantly affects the C3-C4 bond properties in the present system.

A herringbone arrangement was observed in the assembly of benzothieno[2,3-*b*]benzothiophene (**3f**), which is considered to be responsible for its excellent charge transport properties.¹³ The packing structure of the benzoselenophene derivative (**3g**) was found to be very similar to that of **3f** (see the Supporting Information), whereas the benzofuran (**3e**) and benzotellurophene (**3h**) derivatives adopted different packing structures. This difference may be attributed to the atomic radius of the chalcogens. The difference in the sizes of the Se (1.16 Å) and S (1.02 Å) atoms is not as much as that between the sizes of O (0.73 Å) and Te (1.36 Å).¹⁴ In the case of Group 15-heteroacenes, no herringbone motif was observed, probably due to the presence of a peripheral phenyl group. The packing geometry of the arsindole derivative (**3c**) was very close to that of the phosphindole derivative (**3b**), which may also be correlated with the atomic radius.¹⁴



Fig. 2. Top views (top) and side views (bottom) of 3 in the solid state (50% probability level); the

disordered atoms and hydrogen atoms are omitted for clarity. One of two geometries in the unit cell was

drawn for 3d.

The photophysical properties of the present benzothiophene-fused benzoheteroles were evaluated using ultraviolet (UV) absorption spectroscopy; the spectra are shown in Fig. 3, and the photophysical data are summarized in Table 1. The λ_{max} of Group 16-heteroacenes **3e-h** was systematically shifted toward the red region (by ca. 10 nm) on going from O to Te, while the Group 15-heteroacenes did not exhibit such a spectral shift. These spectral changes are very similar to those of the non-fused benzoheteroles.^{7b} The red shift of the Group 16-heteroacenes suggests that the conjugated system is extended by the heteroatoms. Interestingly, a linear relationship was found between the excitation energies for the lowest-energy transition of the Group 16-heteroacenes (**3e-h**) and their atomic radius¹⁴ (Fig. 4). Such a linear relationship was also observed for heteroles, benzoheteroles, and other related heterocyclic systems. Judging from the slopes of the least square lines, the effect of the chalcogen atom on the spectral red-shift decreases with the fusion of benzene and benzothiophene.

To further understand the red-shift observed for the Group 16-heteroacenes, DFT calculations¹⁵ and electrochemical measurements were performed (Table 1 and Fig. 5). Geometry optimization calculations were carried out for all the heteroacenes at the B3LYP/6-311G* (SDD for As, Sb, Se, and Te) level of theory, and the accuracy of the optimized structures were assessed by comparison with the X-ray analysis-derived structures. As shown in the Supporting Information, all the HOMOs and LUMOs are derived from π orbitals of the tetracyclic heteroacene skeletons. It is evident that the HOMO-LUMO energy gap ($\Delta E_{\rm HL}$) decreases as the size of the chalcogen atom increases. The decrease in $\Delta E_{\rm HL}$ was not seen in the Group 15-heteroacenes. These results correlate well with the optical properties observed for the heteroacenes. The destabilization of the HOMO energy for the Group 16-heteroacenes with the larger chalcogen atom was experimentally confirmed by measuring the first oxidation potentials ($E_{\rm pa}$). The largest potential difference (0.74 V vs Fc/Fc⁺) was observed between the E_{pa} values of the benzofuran derivative (1.17 V) and benzotellurophene derivative (0.43 V).



Fig. 3. UV absorption spectra of the Group 15- (a) and 16-heteroacenes (b) in MeOH.

	М	λ_{max} $(nm)^{a}$	$10^{-3} \varepsilon$ $(M^{-1}cm^{-1})^{a}$	$E_{\rm HOMO}$ (eV) ^b	E_{LUMO} (eV) ^b	$\Delta E_{\rm HL}$ (eV) ^c
3a	NPh	342	8.2	-5.36	-1.19	4.17
3b	PPh	340	9.5	-5.77	-1.60	4.17
3c	AsPh	339	11	-5.78	-1.60	4.18
3d	SbPh	344	9.6	-5.77	-1.62	4.15
3e	0	318	24	-5.78	-1.43	4.35
3f	S	329	10	-5.79	-1.50	4.28
3g	Se	335	10	-5.77	-1.54	4.22
3h	Te	349	7.2	-5.67	-1.55	4.12

 Table 1. Photophysical data and calculated HOMO and LUMO levels of 3.

^a From absorption spectra in MeOH. ^b DFT calculation at the level of B3LYP/6-311G* (SDD for As, Se, Sb and Te). ^c Computed HOMO-LUMO gap.



Fig. 4. Plots of atomic radius $(\text{Å})^{14}$ vs experimental excitation energy (cm⁻¹) for the lowest-energy transition for a series of the Group 16-heteroacenes. The excitation energies were based on the λ_{max} values of Table 1. The straight line was drawn using the least-squares method. The excitation energies

for heteroles and benzoheteroles were taken from references 16 and 7b.



Fig. 5. Calculated HOMO and LUMO energy levels for the Group 16-heteroacenes (left) and the contour plots of the HOMO and the first oxidation potentials E_{pa} / (V vs Fc/Fc⁺) (right). The calculations were performed at the level of B3LYP/6-311G* (SDD for Se and Te).

3. Conclusion

In conclusion, we demonstrated a novel divergent synthesis of a series of benzothiophene-fused benzoheteroles containing 15 16 elements from Group and one common precursor, 3-bromo-2-(2-bromophenyl)benzo[b]thiophene (2b), and performed the first systematic comparison of these structures and properties. X-ray single crystal structural analysis showed that the tetracyclic heteroacene skeletons are planar and that the P, As, and Sb atoms are tetrahedrally coordinated. We clarified that the size of the heteroatom incorporated in the heteroacene skeletons strongly affects the packing structures and physicochemical properties. As heavier heteroatoms were introduced, the Group

16-heteroacenes systematically displayed greater red-shift and higher HOMO energy levels. We believe that such polycyclic heteroacenes offer a new perspective for the design of new types of functional π -electron materials for organic electronics applications.

4. Experimental section

4.1. General procedures

Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and are not corrected. ¹H NMR (TMS: δ : 0.00 as an internal standard) and ¹³C NMR (CDCl₃: δ : 77.00 as an internal standard) spectra were recorded on a JEOL JNM-AL400 or JNM-PMX60_{SI} (400 MHz and 100 MHz) spectrometer in CDCl₃ unless otherwise stated. Mass spectra (MS) were obtained on a JEOL JMS-SX-102A instrument. Elemental analyses were performed on MT-5 elemental analyzer (Yanagimoto). IR spectra were recorded on a FT-720 system from HORIBA spectrometer and are reported in frequency of absorption (cm⁻¹). Only selected IR peaks are reported. All manipulations involving air- and/or moisture-sensitive compounds were carried out with the standard Schlenk technique under an argon atmosphere. All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel Pre-coated TLC plates Sil G25 UV₂₅₄. Most of reagents were used without further purification unless otherwise specified. Benzo[b]furan 2a was prepared according to the reported procedures.^{8, 17}

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4.2. Experimental procedures and data of synthetic intermediates

4.2.1. 1-Bromo-2-[(2-methylthiophenyl)ethynyl]benzene (1b). То solution of а 1-iodo-2-(methylthio)benzene (19.4 g, 77.4 mmol, 1.2 eq.) in diethylamine (130 mL), PdCl₂(PPh₃)₂ (445 mg, 0.63 mmol, 1.0 mol%), CuI (499 mg, 2.6 mmol, 4.1 mol%) and 2-bromophenyl acetylene (11.5 g, 63.5 mmol) were added at 0 °C, and stirred for 15 min. The reaction mixture was stirred for 15 h at room temperature, concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ (300 mL) and H₂O (200 mL). The mixture was filtered over Celite and extracted with CH₂Cl₂ (200 mL \times 2). The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane/CH₂Cl₂ (5:1) as eluent to give **1b** as pale yellow prisms (16.4 g, 85% yield): mp 61-63 °C (from hexane/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.61 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 6.9 Hz, 1H), 3.34-7.27 (m, 2H), 7.19 (d, J = 7.8 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 2.52 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 141.9 (C), 133.5 (CH), 132.7 (CH), 132.5 (CH), 129.5 (CH), 129.1 (CH), 127.0 (CH), 125.4 (C), 125.3 (C), 124.3 (CH), 124.2 (CH), 121 (C), 94.1 (C), 91.3 (C), 15.2 (CH₃); IR (KBr): v 2216 (C=C) cm⁻¹; HRMS-EI (m/z): calcd for C₁₅H₁₁BrS [M]⁺ 301.9765, found 301.9774; Anal. Calcd for C₁₅H₁₁BrS: C, 59.42; H, 3.66, found: C, 59.58; H, 3.79.

4.2.2. 3-Bromo-2-(2-bromophenyl)benzo[b]thiophene (2b). A solution of bromine (5.0 g, 31.3 mmol) in CH₂Cl₂ (20 mL) was added dropwise to a solution of 1b (4.70 g, 15.5 mmol) in CH₂Cl₂ (40 mL) for 45

min at 0 °C and stirred for 30 min. After stirred for 1 h at room temperature, to the reaction mixture was added CH₂Cl₂ (150 mL) and saturated sodium thiosulfate (200 mL) at 0 °C, and filtrated over Celite. The filtrate was extracted with CH₂Cl₂ (150 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane/CH₂Cl₂ (20:1) as eluent to give **2b** as colorless prisms (5.29 g, 92% yield): mp 75-79 °C (from hexane/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.52-7.39 (m, 4H), 7.33 (t, *J* = 7.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 138.4 (C), 137.9 (C), 137.3 (C), 134.1 (C), 133.0 (CH), 132.5 (CH), 130.7 (CH), 127.2 (CH), 125.7 (CH), 125.2 (CH), 124.6 (C), 123.6 (CH), 122.3 (CH), 108.6 (C); HRMS-EI (*m*/*z*): calcd for C₁₄H₈Br₂S [M]⁺ 365.8713, found 365.8679; Anal. Calcd for C₁₄H₈Br₂S: C, 45.68; H, 2.19, found C, 45.13; H, 2.33. Spectroscopic data are in accordance with the literature.¹⁸

4.3. Experimental procedures and data of 10-phenyl[1]benzothieno[3,2-b]indole (3a)

The mixture of aniline (47 mg, 0.51 mmol), **2b** (203 mg, 0.55 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (33 mg, 0.11 mmol, 22 mol%), sodium *tert*-butoxide (160 mg, 1.67 mmol), and tris(dibenzylideneacetone)dipalladium (101 mg, 0.11 mmol, 22 mol%) in toluene (5 mL) was stirred for 30 min at room temperature. The sealed reaction tube was then heated to 125 °C for 24 h. The mixture was cooled to room temperature, diluted with CH_2Cl_2 and water at 0 °C, and filtered over Celite. The filtrate was extracted with CH_2Cl_2 . The combined organic layer was washed with brine, dried over

anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane/CH₂Cl₂ (20:1) as eluent to give **3a** as yellow prisms (107 mg, 71% yield): mp 111-114 °C (from ethanol/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.64-7.52 (m, 5H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.30-7.17 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 143.1 (C), 142.5 (C), 137.9 (C), 137.5 (C), 129.7 (CH), 128.2 (CH), 127.7 (CH), 126.8 (C), 124.3 (CH), 124.0 (CH), 123.9 (CH), 123.4 (CH), 122.1 (C), 120.5 (CH), 120.4 (CH), 119.3 (CH), 116.8 (C), 111.0 (CH); HRMS-EI (*m*/*z*): calcd for C₂₀H₁₃NS [M]⁺ 299.0769, found 299.0769; Anal. Calcd for C₂₀H₁₃NS: C, 80.23; H, 4.38; N, 4.68, found C, 80.27; H, 4.72; N, 4.70. Spectroscopic data are in accordance with the literature.³⁴

4.4. General procedure of [1]benzothieno[3,2-b][1]benzoheteroles (3b-h)

A solution of BuLi was added dropwise to a solution of **2** (2.0 mmol) in diethyl ether 40 mL at -20 °C (for **3b-d**, **f-h**) or -78 °C (for **3e**) and stirred. After 15 min, to the reaction mixture Group 15 or 16 reagent (4 mmol) was added and the resulting mixture was gradually raised to room temperature and stirred for 15 h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and water (100 mL), and filtrated over Celite. The filtrate was extracted with CH_2Cl_2 (100 mL × 2). The combined organic layer was washed with brine (200 mL × 2), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane/CH₂Cl₂.

4.4.1. 10-Phenyl[1]phosphindolo[3,2-b][1]benzothiophene (3b). Following the general procedure, with 2b, a solution of 1.75 M *n*-BuLi in hexane (3.1 mL, 4.8 mmol), and dichlorophenylphosphine (718 mg, 4.0 mmol) afforded compound 3b as colorless prisms (430 mg, 68% yield); mp 133-137 °C (from methanol/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.89 (d, J = 8.2 Hz, 1H), 7.73-7.67 (m, 3H), 7.45-7.22 (m, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ 148.3 (C, d, $J_{c,p} = 3.8$ Hz), 146.0 (C, d, $J_{c,p} = 4.8$ Hz), 143.0 (C, d, $J_{c,p} = 4.8$ Hz), 139.6 (C, d, $J_{c,p} = 1.9$ Hz), 138.1 (C, d, $J_{c,p} = 6.7$ Hz), 138.1 (C, d, $J_{c,p} = 17.3$ Hz), 133.9 (C, d, $J_{c,p} = 17.3$ Hz), 132.8 (CH, d, $J_{c,p} = 21.1$ Hz), 130.2 (CH, d, $J_{c,p} = 21.1$ Hz), 129.5 (CH), 128.8 (CH, d, $J_{c,p} = 7.7$ Hz), 128.7 (CH, d, $J_{c,p} = 8.6$ Hz), 126.8 (CH, d, $J_{c,p} = 8.6$ Hz), 125.0 (CH), 124.5 (CH), 123.6 (CH), 123.0 (CH), 121.7 (CH); HRMS-EI (*m*/z); calcd for C₂₀H₁₃PS [M]⁺ 316.0476, found 316.0473; Anal. Calcd for C₂₀H₁₃PS: C, 75.93; H, 4.14, found C, 75.57; H, 4.36. Spectroscopic data are in accordance with the literature.^{4b}

4.4.2. 10-Phenyl[1]benzoarsolo[3,2-b][1]benzothiophene (3c). Following the general procedure, with **2b**, a solution of 1.75 M *n*-BuLi in hexane (3.1 mL, 4.8 mmol), and dichlorophenylarsine (890 mg, 4.0 mmol) afforded compound **3c** as colorless prisms (562 mg, 78% yield); mp 118-120 °C (from methanol/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.89 (d, J = 7.3 Hz, 1H), 7.75 (d, J = 6.9 Hz, 1H), 7.68 (t, J = 7.8 Hz, 2H), 7.42 (t, J = 6.9 Hz, 1H), 7.34-7.16 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.9 (C), 148.2 (C), 142.4 (C), 141.4 (C), 140.7 (C), 139.5 (C), 138.3 (C), 132.3 (CH), 131.3 (CH), 128.9 (CH), 128.8 (CH), 127.1 (CH), 125.0 (CH), 124.4 (CH), 123.4 (CH), 123.4 (CH), 122.5 (CH);

HRMS-EI (*m*/*z*): calcd for C₂₀H₁₃AsS [M]⁺ 359.9954, found 359.9948; Anal. Calcd for C₂₀H₁₃AsS: C, 66.67; H, 3.64, found C, 66.44; H, 3.80.

4.4.3. 10-Phenyl[1]benzostibolo[3,2-b][1]benzothiophene (3d). Following the general procedure, with **2b**, a solution of 1.75 M *n*-BuLi in hexane (3.1 mL, 4.8 mmol), and dibromophenylstibane (1.43 g, 4.0 mmol) afforded compound **3d** as colorless prisms (585 mg, 72% yield); mp 100-102 °C (from hexane/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.89 (d, *J* = 6.9 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.43-7.14 (m, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ 156.1 (C), 145.4 (C), 145.4 (C), 142.6 (C), 141.4 (C), 139.4 (C), 137.4 (C), 135.3 (CH), 134.8 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 127.4 (CH), 124.9 (CH), 124.4 (CH), 124.3 (CH), 123.7 (CH), 123.0 (CH); HRMS-EI (*m*/*z*): calcd for C₂₀H₁₃SbS [M]⁺ 405.9776, found 405.9770; Anal. Calcd for C₂₀H₁₃SbS: C, 59.00; H, 3.22, found C, 58.87; H, 3.37.

4.4.4. [1]Benzothieno[3,2-b][1]benzofuran (3e). Following the general procedure, with 2a, a solution of 1.05 M *t*-BuLi in hexane (7.6 mL, 8.0 mmol), and bis(phenylsulfonyl)sulfide (1.25 g, 4 mmol) afforded compound 3e as colorless prisms (245 mg, 55% yield): mp 132-134 °C (from hexane/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 8.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 158.8 (C), 153.0 (C), 142.0 (C), 125.1 (C), 124.9 (CH), 124.9 (CH), 124.3 (CH), 124.0 (C), 123.3 (CH), 119.7 (CH), 119.6 (CH), 118.6 (C), 112.5 (CH); HRMS-EI (*m/z*): calcd for

 $C_{14}H_8OS [M]^+$ 224.0296, found 224.0297; Anal. Calcd for $C_{14}H_8OS$: C, 74.97; H, 3.60, found C, 74.99; H, 3.65. Spectroscopic data are in accordance with the literature.^{3d}

4.4.5. [1]Benzothieno[3,2-b][1]benzothiophene (3f). Following the general procedure, with 2b, a solution of 1.75 M *n*-BuLi in hexane (3.1 mL, 4.8 mmol), and bis(phenylsulfonyl)sulfide (1.25 g, 4.0 mmol) afforded compound 3f as colorless prisms (312 mg, 65% yield); mp 215-219 °C (from hexane/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 142.2 (C), 133.4 (C), 133.1 (C), 125.0 (CH), 124.9 (CH), 124.0 (CH), 121.6 (CH); HRMS-EI (*m*/*z*): calcd for C₁₄H₈S₂ [M]⁺ 240.0067, found 240.0067; Anal. Calcd for C₁₄H₈S₂: C, 69.96; H, 3.36, found C, 70.04; H, 3.64. Spectroscopic data are in accordance with the literature.^{2c}

4.4.6. [1]Benzoselenolo[3,2-b][1]benzothiophene (3g). Following the general procedure, with 2b, a solution of 1.75 M *n*-BuLi in hexane (3.1 mL, 4.8 mmol), and bis(phenylsulfonyl)selenide (1.44 g, 4.0 mmol) afforded compound 3g as red prisms (379 mg, 66% yield); mp 206-209 °C (from ethanol/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.94 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.3 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 142.1 (C), 141.2 (C), 135.7 (C), 135.6 (C), 135.2 (C), 131.7 (C), 127.0 (CH), 125.3 (CH), 125.2 (CH), 124.9 (CH), 124.9 (CH), 123.8 (CH), 123.1 (CH), 122.2 (CH); HRMS-EI (*m*/*z*): calcd for C₁₄H₈SSe [M]⁺ 287.9512, found 287.9505;

Anal. Calcd for $C_{14}H_8SSe$: C, 58.54; H, 2.81, found C, 58.71; H, 3.08. Spectroscopic data are in accordance with the literature.^{2c}

4.4.7. [1]Benzotellurolo[3,2-b][1]benzothiophene (**3h**). Following the general procedure, with **2b**, a solution of 1.75 M *n*-BuLi in hexane (3.1 mL, 4.8 mmol), and tellurium powder (522 mg, 4.0 mmol) afforded compound **3h** as pale yellow needles (343 mg, 51% yield); mp 164-166 °C (from methanol/CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.3 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.40-7.36 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 141.8 (C), 140.1 (C), 139.9 (C), 139.6 (C), 133.1 (CH), 130.9 (C), 126.1 (CH), 125.3 (CH), 125.1 (CH), 124.9 (CH), 123.5 (CH), 123.4 (CH), 119.2 (C); HRMS-EI (*m*/*z*): calcd for C₁₄H₈STe [M]⁺ 337.9407, found 337.9419; Anal. Calcd for C₁₄H₈STe: C, 50.06; H, 2.40, found C, 50.08; H, 2.58.

4.5. Cyclic voltammograms

Electrochemical measurements were conducted on a HZ-3000 voltammetric analyzer (Hokuto Denko) under argon atmosphere in a CH_2Cl_2 solution of tetrabutylammonium perchlorate (0.1 M). A glassy carbon electrode was used as a working electrode, a platinum-wire was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. The CV curves were calibrated using the ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an external standard which was measured under the same conditions after the measurement of samples.

4.6. X-ray crystallographic data

The X-ray diffraction measurements of compounds **3** were carried out using a Rigaku AFC-8 with Saturn70 CCD using Mo K α radiation ($\lambda = 0.71073$ Å). The CrystalClear program was used for absorption correction. The structure was solved by direct methods using SIR2004 (for **3a-f**, **h**) or SHELXL-97¹⁹ (for **3g**), followed by successive refinements using the full-matrix least-squares method on F^2 using SHELXL-97.²⁰ All the nonhydrogen atoms were refined anisotropically, whereas the hydrogen atoms were refined isotropically.

The experimental and refinement details of the X-ray crystallographic structures of compound can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk), CCDC #1481568 to 1481575 for **3a-3h**, respectively.

4.7. Computational details

All calculations were performed at the DFT level, by means of the B3LYP functional as implemented in Gaussian 09.¹⁵ The 6-311G* basis sets were used for H, C, N, O, P, and S atoms, while the SDD basis sets were applied for As, Se, Sb, and Te atoms. X-ray structures of **3a-3h** were used as initial structures for geometry optimization calculations. Vibrational frequency computations verified the nature of the stationary points.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at XXX

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