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General Synthesis of Thiophene and Selenophene-Based Heteroacenes

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ABSTRACT

A new intramolecular triple cyclization of bis(*o*-haloaryl)diacetylenes, via dilithiation followed by reaction with chalcogen elements, produces π-conjugated compounds containing heterole–1,2-dichalcogenin–heterole fused tricyclic skeletons. The subsequent dechalcogenation with copper metal affords a series of thiophene- and selenophene-based heteroacenes.

Fused polycyclic aromatic hydrocarbons (PAHs) are an important class of molecules as fundamental skeletons for functional organic materials.[1] Their rigid π-conjugated frameworks, free from conformational disorder, are a decisive characteristic leading to unique electronic properties. A representative example is a linearly fused acene such as pentacene.[2,3] The flat π-conjugated framework realizes densely packed solid-state structures that are beneficial in achieving high carrier mobility. This class of molecules is currently among the most extensively investigated materials for organic thin film transistors.[4] In this context, thiophene- and selenophene-based heteroacenes are also of interest,[5−9] since the heteroatom effects not only on the electronic structures but also on the solid-state structures[10] would make

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[1] (a) Harvery, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997. (b) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267.

[2] (a) Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854. (b) Brédas, J. L.; Calbert, J. P.; da Silva Filho; D. A.; Cornil, J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5804. (c) Mattheus, C. C.; de Wijs, G. A.; de Groot, R. A.; Palstra, T. T. M. *J. Am. Chem. Soc.* **2003**, *125*, 6323. (d) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. *J. Am. Chem. Soc.* **2004**, *126*, 7416.

[3] (a) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876. (b) Anthony, J. E.; Brooks, J. S.; Eaton, D. A.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (c) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028. (d) Perepichka, D. F.; Bendikov, M.; Meng, H.; Wudl, F. *J. Am. Chem. Soc.* **2003**, *125*, 10190. (e) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138. (f) Chan, S. H.; Lee, H. K.; Wang, Y. M.; Fu, N. Y.; Chen, X. M.; Cai Z. W.; Wong, H. N. C. *Chem. Commun.* **2005**, 66.

[4] (a) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (b) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359.

[5] (a) Schroth, W.; Hintzsche, E.; Viola, H.; Winkler, R.; Klose, H.; Boese, R.; Kempe, R.; Sieler, J. *Chem. Ber.* **1994**, *127*, 401. (b) Schroth, W.; Hintzsche, E.; Felicetti, M.; Spitzner, R.; Sieler, J.; Kempe, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 739. (c) Schroth, W.; Hintzsche, E.; Jordan, H.; Jende, T.; Spitzner, R.; Thondorf, I. *Tetrahedron* **1997**, *53*, 7509.

[6] (a) Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. 2* **1992**, 761. (b) Sato, N.; Mazaki, Y.; Kobayashi, K.; Kobayashi, T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 765.

[7] Zhang, X.; Côté, A. P.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 10502.

[8] Oyaizu, K.; Iwasaki, T.; Tsukahara, Y.; Tsuchida, E. *Macromolecules* **2004**, *37*, 1257.

[9] Other thiophene-based heteroacenes: (a) Li,. X.-C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 2206. (b) Rajca, R.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481. (c) Zhang, X.; Matzger, A. J. *J. Org. Chem.* **2003**, *68*, 9813. (d) Nenajdenko, V. G.; Sumerin, V. V.; Chernichenko, K. Y.; Balenkova, E. S. *Org. Lett.* **2004**, *6*, 3437.

[10] Werz, D. B.; Gleiter, R.; Rominger, F. *J. Am. Chem. Soc.* **2002**, *124*, 10638.

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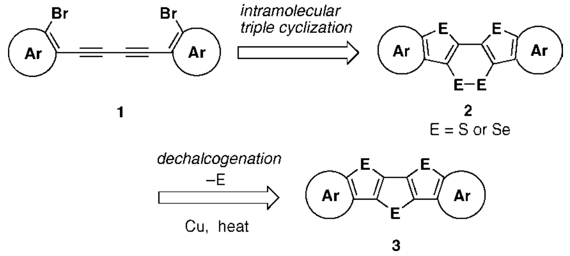
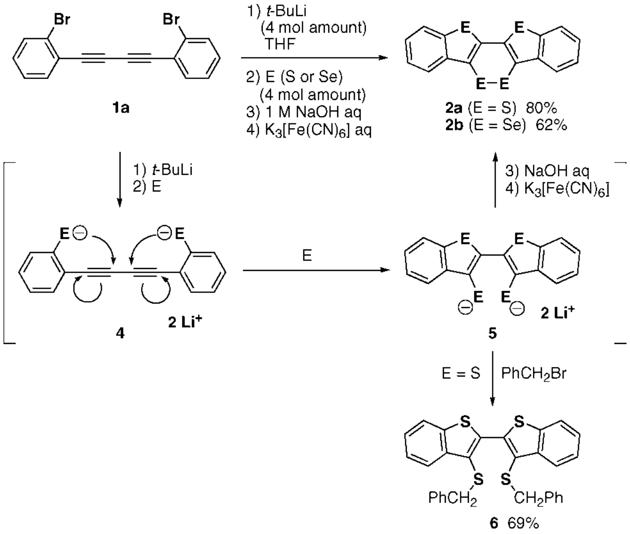
Scheme 1. General Scheme for the Synthesis of Heteroacenes



Scheme 2. Intramolecular Triple Cyclization



them more attractive candidates. However, only a limited number of this class of molecules have been reported to date, such as dibenzo-annulated dithieno[3,2-*b*:2′,3′-*d*]thiophene,[5] fused oligothiophenes consisting of five or seven thiophene rings,[6,7] and a fully fused polythiophene.[8] This may be due to a lack of useful synthetic routes in terms of efficiency as well as accessible structural diversity. The exploration of conceptually new methodology is thus a compelling subject in this chemistry.

We now report a general and facile synthetic route to the thiophene- and selenophene-containing heteroacenes based on a new intramolecular triple cyclization of bis(*o*-haloaryl)-diacetylenes **1**, as shown in Scheme 1. This cyclization constructs a heterole−1,2-dichalcogenin−heterole fused tricyclic skeleton in one pot. The subsequent dechalcogenation with copper metal[5] produces a series of thiophene- and selenophene-based heteroacenes. The structures and fundamental properties of the fused 1,2-dichalcogenin compounds **2** and the heteroacenes **3** are also described in this Letter.

A typical example of the intramolecular triple cyclization with bis(*o*-bromophenyl)diacetylene **1a** as a starting material is shown in Scheme 2. This cyclization involves three reaction steps. The first step is the dilithiation of **1a** with *t*-BuLi in THF, followed by trapping with a chalcogen element (4 mol amounts) to produce a dianionic intermediate **4**. In the second step, the dianion centers attack on the inner carbon atoms of the diacetylene moiety, followed by trapping with the remaining chalcogen element to afford a doubly cyclized intermediate **5**. Then, through the counterion exchange of lithium with sodium by the addition of 1 M NaOH aqueous solution, and in the final step, potassium ferricyanide(III) is employed as an oxidant to convert **5** to the target heteroacene, according to Schroth's report.[5] This sequential procedure affords fused thiophene derivative **2a** or selenophene derivative **2b** in good yields.

There are several features for the present cyclization: (1) The cyclization proceeds via an anionic mechanism. This is supported by a trapping of the intermediate **5** with benzyl bromide, which produces a corresponding bis(benzylthio) compound **6** in 69% yield. (2) There are two important precedent reactions related to the present cyclization: that is, the heteroannulation of (*o*-alkynylphenyl)thiolate to benzothiophene via a 5-*endo-dig* cyclization[11] and the oxidation of 2,2′-bithiophene-3,3′-dithiolate to dithieno-fused 1,2-dithiin.[5] Notably, the simple idea of employing of the diacetylenic compound as a starting material allows us to achieve the facile one-pot synthesis of the fused tricyclic structure via the two aforementioned transformations. (3) The present cyclization proceeds in a regiospecific manner. No other regioisomer, in terms of the position of a six-membered dichalcogenin ring, was obtained. (4) The cyclization proceeds well, not only with sulfur, but also with selenium. This is the first synthesis of fused polycyclic diselenin compounds.

On the basis of this procedure, a series of fused 1,2-dichalcogenin π-electron systems, including not only benzo-annulated derivatives **2a**−**d**, but also thieno- or benzothieno-annulated derivatives **2e**−**g**, were synthesized from appropriate diacetylenes,[12] as shown in Scheme 3.

Schroth has already reported the copper-mediated dechalcogenation from 1,2-dithiin **2a** to **3a** at high temperature.[5a] In a similar manner, the produced 1,2-dichalcogenin derivatives **2b**−**g** were successfully converted into the corresponding heteroacenes **3b**−**g** (Scheme 3). Whereas some of the dichalcogenin derivatives have very poor solubility, the reaction can be conducted only by heating a mixture of powdered **2** and Cu nanopowder (ca. 100 nm) without use of any solvent. The reaction starts upon melting of the dichalcogenin at ca. 250−350 °C and finishes within a few minutes. The subsequent purification by recrystallization or sublimation affords pure heteroacene compounds. The newly produced heteroacenes **3** were identified with use of NMR spectroscopies and elemental analysis, except for the seven-ring-fused derivatives **3f** and **3g**, which have almost no solubility toward common organic solvents at ambient temperature and could not be chracterized by the NMR spectroscopy. All the product compounds are very stable toward heat and light and can be handled without special care.

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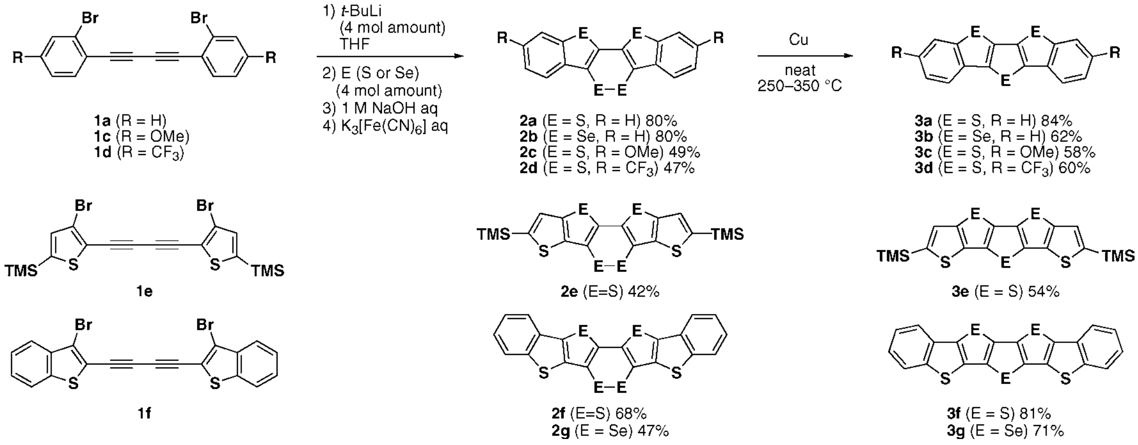
[11] For example, see: Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5084.

[12] The starting diacetylenes were readily synthesized in three steps from appropriate bromoiodoarenes, via the Pd/Cu-catalyzed coupling with $Me_3SiC{\equiv}CH$, alkaline desilylation, and Cu-mediated homocoupling.

Scheme 3. Synthesis of a Series of Fused 1,2-Dichalcogenins and Heteroacenes



Among the produced compounds, the crystal structures of **2b** and **3a** have been determined by X-ray crystallography.[13] As shown in Figure 1, while the six-membered 1,2-diselenin ring is highly deviated from a planar structure with a C−Se−Se−C dihedral angle of 52°, heteroacene **3a** has a nearly coplanar structure. Notably, this compound forms a herringbone packing structure that is very similar to that of pentacene.[14] Considering this similarity, the investigation on their solid-state properties, such as a carrier mobility, would give important information about the structure−properties relationships.[15] Further research along this line is in progress.

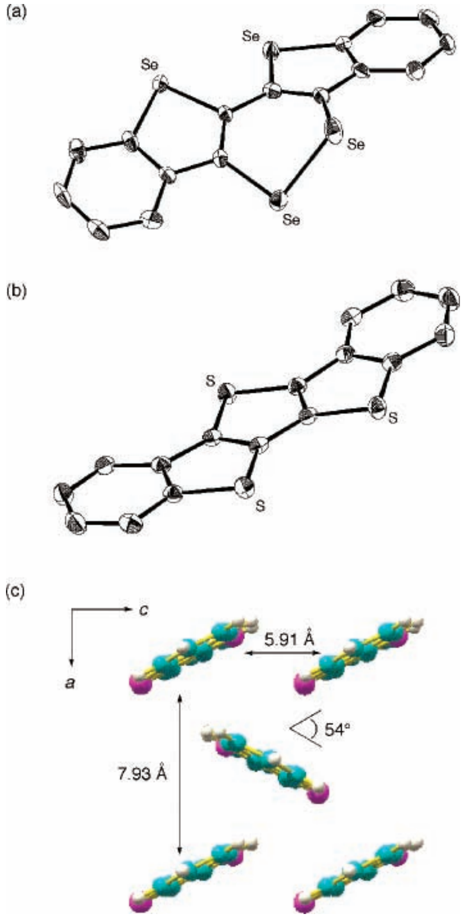


Figure 1. ORTEP drawings of (a) **2b** and (b) **3a** (50% probability for thermal ellipsoids) and (c) packing structure of **3a**.

The photophysical and electrochemical data for the fused 1,2-dichalocogenin compounds **2** and the heteroacenes **3** are collected in Table 1.

In UV−visible absorption spectra, while the fused 1,2-dichalcogenin π-systems **2** have weak absorption bands with maximum wavelengths around 460−520 nm, together with intense structureless $\pi-\pi^*$ transition bands with maxima around 330−380 nm, the heteroacenes **3** show vibronic $\pi-\pi^*$ transition bands with the longest absorption maxima around 340−420 nm (for detailed data, see the Supproting Information). For example, the absorption spectra of **2e** and **3e** are shown in Figure 2a. According to the preliminary TDDFT calculation of **2e** with 6-31G(d) basis sets (λ_{calc}, 545 nm, f = 0.1414), its long wavelength absorption band observed at 473 nm is assignable to the transition from the HOMO consisting of the n−π conjugation between the lone pair electrons on the chalcogen element and the π-conjugated framework (Figure 2c) to the LUMO mainly consisting of the S−S σ^* orbital.

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(13) Crystallographic data: **2b**: $C_{16}H_8Se_4$, FW = 516.06, crystal dimensions 0.20 × 0.20 × 0.20 mm^3, monoclinic, space group $P2_1/a$, a = 12.632(8) Å, b = 7.864(4) Å, c = 14.964(10) Å, β = 101.258(7)°, V = 1457.8(15) Å^3, Z = 4, D_c = 2.351 Mg m^{-3}, μ(Mo Kα) = 10.050 mm^{-1}, T = 173(2) K, F(000) = 960, $2\theta_{\max}$ = 50°. 8281 reflections measured, of which 2467 were unique. Final R_1 = 0.0510 with wR_2 = 0.1309 for 2467 observed reflections with $I > 2\sigma(I)$. **3a**: $C_{16}H_8S_3$, FW = 296.40, crystal dimensions 0.20 × 0.20 × 0.02 mm^3, orthorhombic, space group $Pnma$, a = 7.933(4) Å, b = 26.589(15) Å, c = 5.906(3) Å, V = 1245.9(11) Å^3, Z = 4, D_c = 1.580 Mg m^{-3}, μ(Mo Kα) = 0.573 mm^{-1}, T = 173(2) K, F(000) = 608, $2\theta_{\max}$ = 55°. 6907 reflections measured, of which 1110 were unique. Final R_1 = 0.0417 with wR_2 = 0.0913 for 1110 observed reflections with $I > 2\sigma(I)$.

(14) Holmes. D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399.

(15) (a) Brédas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J. *Proc. Natl. Acad. Sci.* **2002**, *99*, 5804. (b) Curtis, M. D.; Cao, J.; Kampf, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 4318.

Table 1. Photophysical and Electrochemical Data for Fused 1,2-Dichalcogenins **2** and Heteroacenes **3**

	UV−vis absorption[a]		redox potential[b]		
compd	λ_{max}/nm[c]	log ϵ	$E_{1/2,ox1}$/V	$E_{1/2,ox2}$/V	E_{pc}/V
2a[d]	468	3.41	+0.72	+1.08	−1.54
2b[d]	498	2.12	+0.64	+1.03	−1.46
2c[d]	473	3.56	+0.54	+0.80	−1.51
2d[d]	471	3.49	+0.87	+1.22	−1.37
2e[d]	473	3.81	+0.63	+0.91	−1.46
2f[e]	480	3.99	+0.67	+1.02	−1.53
2g[e]	516	3.51	+0.62	+0.99	−1.45
3a[d]	344	4.51	+0.99	*f*	*f*
3b[e]	356	4.56	(+0.90)[g]	*f*	*f*
3c[e]	356	4.43	(+0.43)[g]	*f*	*f*
3d[d]	350	4.59	+1.30	*f*	*f*
3e[d]	370	4.65	+0.68	*f*	*f*
3f	399[h]	3.98	*i*		
3g	418[h]	3.08	*i*		

[a] In THF, unless otherwise stated. [b] Determined by cyclic voltammetry (CV) under the following condition: Sample 1 mM; *n*-Bu_4NPF_6 (0.1 M) in PhCN or *o*-dichlorobenzene. Potentials are given against the ferrocene/ferrocenium couple (Fc/Fc^+). While all reduction waves were irreversible, all oxidation processes were reversible unless otherwise stated. [c] Only the longest absorption maximum wavelengths are given. [d] CV measured in PhCN. [e] CV measured in *o*-dichlorobenzene. [f] Not observed. [g] Irreversible process. Oxidation peak potential (E_{pa}) is given in the parentheses. [h] Measured in CS_2. [i] Could not be obtained due to poor solubiliy of the sample.

In the cyclic voltammetry, both of the fused dichalcogenin compounds **2** and heteroacenes **3** (except for **3b** and **3c**) show reversible oxidation waves at rather low oxidation potentials. For example, while **3e** shows one reversible oxidation wave at $E_{1/2} = +0.68$ V (vs Fc/Fc^+), **2e** shows two reversible oxidation waves at +0.63 and +0.91 V, as shown in Figure 2b. Considering the 1,2-dichalcogenin ring as the 8π-electron system with two sets of lone pair electrons on the chalcogen atoms, the redox stability of the 1,2-dichalcogenin systems may be rationalized by thinking the aromatic stabilization in the resultant two-electron oxidized 6π-electron species. In both series of compounds **2a**−**d** and **3a**−**d**, the oxidation potential can be tuned by the substituents R, while the substituent effect is more significant in the heteroacenes series. All these results indicate the potential utility of the heteroacenes as well as the fused 1,2-dichalcogenin compounds for the electronic applications.

In summary, a new synthetic methodology based on the intramolecular triple cyclization of bis(*o*-haloaryl)diacetylenes opens the door to the general synthesis of fused dichalcogenin π-electron systems and heteroacenes. This achievement will be relevant to further progress in this field.

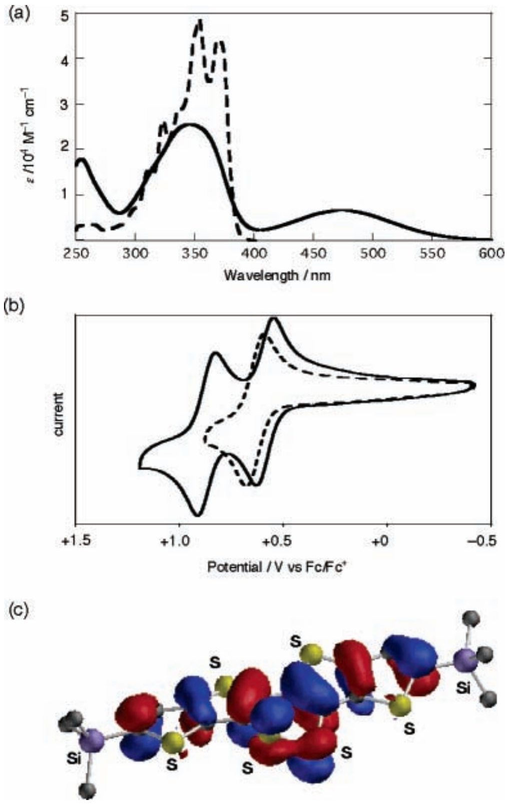

Figure 2. Comparisons between fused 1,2-dichalcogenin compound **2e** (solid line) and heteroacene **3e** (dashed line) in (a) UV−vis absorption spectra in THF and in (b) cyclic voltammograms and (c) Kohn−Sham HOMO of **2e** calculated at the B3LYP/6-31G(d) level.

Further studies on the applications of these materials to electronic devices such as thin film transistors, as well as the synthesis of more extended heteroacenes, are in progress in our laboratory.

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Supporting Information Available: Experimental procedures and spectral data for **1**−**3**, and crystallographic data for **2b** and **3a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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