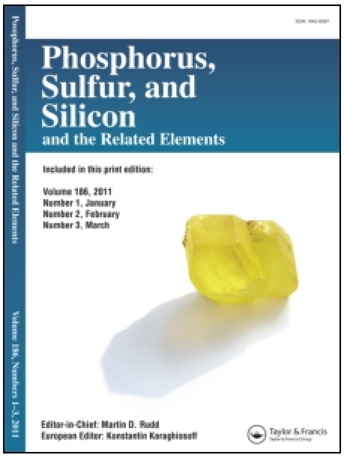

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Selenium-Containing π-Conjugated Compounds for Electronic Molecular Materials

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To cite this Article Takimiya, Kazuo and Otsubo, Tetsuo(2005) 'Selenium-Containing π-Conjugated Compounds for Electronic Molecular Materials', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 3, 873 — 881

To link to this Article: DOI: 10.1080/10426500590906373

URL: http://dx.doi.org/10.1080/10426500590906373

Phosphorus, Sulfur, and Silicon, 180:873–881, 2005
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590906373

Selenium-Containing π-Conjugated Compounds for Electronic Molecular Materials

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Novel selenium-containing π-conjugated compounds have been studied for the development of organic metals, superconductors, and field-effect-transistors. Methylenedithiotetraselenafulvalene (MDT-TSF) and its related electron donors are effectively synthesized by the recently developed synthetic method consisting of the one-pot formation of 1,3-diselenole-2-selones, the deprotection/realkylation procedure of the protected tetrachalcogenafulvalene-thiolate and -selenolate, and the ring closing reaction via trans-alkylation on sulfur or selenium atom. These new compounds serve as good electron donors for developing not only highly conducting charge-transfer salts (>10^3 S cm^{-1}) but also superconducting salts. Among six selenium-containing methylenedichalcogeno-tetrachalcogenafulvalenes, we found that four of them can produce superconducting salts, indicating that the present compounds are superior class of electron donors.

For the development of high-performance organic semiconductors for organic field effect transistor (OFET) devices, we focused our attention to selenophene-containing acene-type compounds, namely benzo[1,2-b:4,5-b′]diselenophene (BDS) derivatives hitherto unknown. A new synthetic method for BDS derivatives consisting of double heterocycle-formation on the central benzene ring has been established and has made it possible to synthesize a range of BDS derivatives. Among them, 2,6-diphenyl derivative (DPh-BDS) shows very high hole mobility of 0.17 cm^2/Vs, which is classified into the highest class of field-effect mobility of organic thin films.

Received January 30, 2004; accepted October 20, 2004.

We thank Prof. Y. Aso, Prof. T. Mori, Dr. Y. Kunugi, and Dr. T. Kawamoto for collaboration. This work was partially supported by Industrial Technology Research Grant Program in 2003 from New Energy and Industrial Technology Development Organization (NEDO) of Japan and Regional Science Promotion Program Evolutional Research. We also are grateful for financial support from a Grant-in-Aid for Scientific Research on Priority Areas of Molecular Conductors (No. 15073218) from the Ministry of Education, Science, Sports, and Culture, Japan. Kazuo Takimiya is deeply indebted to the Electronic Technology Research Foundation Chugoku for the financial support for attending ICCST-9, Mumbai, India.

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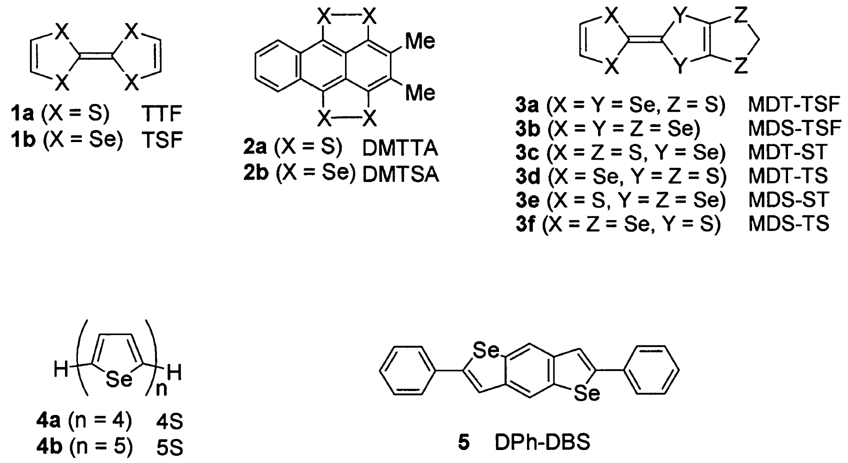
Keywords Electron donor; heterocyclic synthesis; organic superconductor; oligoselenophene

INTRODUCTION

In the field of electronic molecular materials, e.g., organic metals, superconductors, and organic semiconductors, sulfur-containing heterocyclic compounds such as tetrathiafulvalene (TTF)[1–2] and thiophene derivatives[3,4] have played an important role. In general, intermolecular interaction in the solid state is an essential parameter to determine the solid-state properties of the electronic functional materials. Thus, substitution of sulfur atoms in the TTF (**1a**) (Figure 1) and thiophene-based compounds by selenium atoms can be an effective way to improve the physical properties owing to enhanced intermolecular interaction through nonbonded Se–Se contacts in the solid state. This is well exampled by the conductive properties of tetrachalcogenafulvalene-tetracyanoquinodimethane (TCNQ) complexes. TTF-TCNQ complex shows conductivity of 500 S cm^{-1} and metallic temperature dependence down to 59 K, at which temperature a metal-insulator transition takes place owing to the Peierls instability.[5] On the other hand, the TCNQ complex of the selenium analogue, tetraselenafulvalene (**1b**, TSF) shows rather higher conductivity of 800 S cm^{-1} and the metallic state is further stabilized down to 40 K.[6] We also found a similar improvements of the conductive properties in a dichalcogen-bridged anthracene system: the 1:1 radical cation salt of



1a (X = S) TTF
1b (X = Se) TSF

2a (X = S) DMTTA
2b (X = Se) DMTSA

3a (X = Y = Se, Z = S) MDT-TSF
3b (X = Y = Z = Se) MDS-TSF
3c (X = Z = S, Y = Se) MDT-ST
3d (X = Se, Y = Z = S) MDT-TS
3e (X = S, Y = Z = Se) MDS-ST
3f (X = Z = Se, Y = S) MDS-TS

4a (n = 4) 4S
4b (n = 5) 5S

5 DPh-DBS

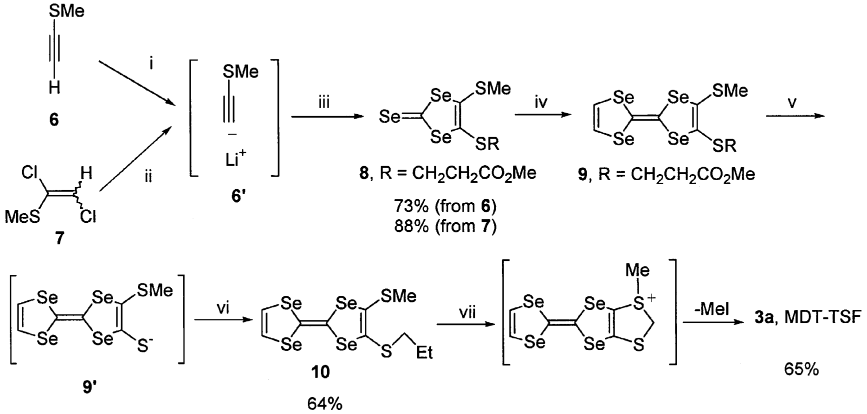
FIGURE 1 Structure of chalcogen containing π-conjugated compounds.

dimethylteterathioanthracenes (**2a**, DMTTA) with BF_4^- anion showed moderate conductivity ($\sigma_{rt} = 7.0$ S cm^{-1}) with semiconductive temperature dependence, whereas the BF_4 salt with selenium donor, dimethylteteraselenoanthracenes (**2b**, DMTSA), is highly conducting at room temperature (450 S cm^{-1}) and shows metallic behavior down to ca. 200 K.[7] These experimental results apparently show that introduction of selenium is very effective for improvement of electronic properties.

Form the viewpoint of synthetic chemistry, however, introduction of selenium atoms into various π-conjugated molecules has been not very easy, because of the lack of suitable synthetic method and reagents.[8] Furthermore, selenium reagents, if available, are more expensive than their sulfur counterparts, and their high toxicity and bad smell are always problematic in synthetic experiments. Therefore, one can imagine that the development of effective synthetic methods and practical protocol for selenium-containing materials greatly contributes to the chemistry of electronic materials. In this article, we will report our recent results on the development of organic superconductors based on selenium-containing methylenedichalcogenotetrachalcogenafulvalenes (**3a–3f**) and organic semiconductors consisting of selenophene-based conjugated molecules (**4** and **5**), in terms of their novel synthetic chemistry and improved electronic properties.

SELENIUM ANALOGUES OF METHYLENEDICHALCOGENOTETRACHALCOGENAFULVALENES (MDX-TXFs) FOR ORGANIC SUPERCONDUCTORS

The synthesis of methylenedithiotetraselenafulvalene (**3a**, MDT-TSF) is shown in Scheme 1, which features three new reactions recently developed for the synthesis of selenium containing TTF derivatives.[9,10] The first reaction is the one-pot synthesis of 4-methylthio-5-(2-methoxycarbonylethylthio)-1,3-diselenole-2-selone;[11] lithium methylthioacetylide (**6′**), generated from methylthiacetylene (**6**) with 1.0 equivalent of buthyllithium or more conveniently 1-methylthio-1,2-dichloroethene (**7**) with 2.0 equivalent of buthyllithium was consequently reacted with selenium powder, carbon diselenide, and finally methyl 3-thiocyanateproponate to give 4-methylthio-5-(2-methoxycarbonylethylthio)-1,3-diselenole-2-selone (**8**). After the conversion of **8** into **9** by a conventional phophite-mediated cross-coupling reaction with the parent 1,3-diselenole-2-selone, treatment of **9** with cesium hydroxide monohydrate in dimethylbranamide (DMF) *in situ* produced the thiolate intermediate (**9′**), which effectively was alkylated



SCHEME 1 Synthesis of MDT-TSF: (i) BuLi (1.0 equiv.); (ii) BuLi; (2.0 equiv.); (iii) Se, CSe_2, $NCS(CH_2)_2CO_2Me$; (iv) 1,3-diselenole-2-selone, $P(OMe_3)$; (v) $CsOH{\cdot}H_2O$; (vi) $BrCH_2Cl$; (vii) NaI.

with bromochloromethane to give **10** in 64% yield.[12,13] Finally, formation of the outer sulfur-containing heterocycle was achieved by a reaction of **10** with sodium iodide; a mixture of **10** and sodium iodide in 2-butanone or 2-pentanone simultaneously effected a halogen-exchange reaction and the transalkylation reaction on the sulfur atom.[14–17] This synthetic method is quite versatile and applicable to various TSF and diselenadithiafulvalene derivatives with outer sulfur- or selenium-containing hetercocycles.[18] The related selenium-containing electron donors **3b–3f** also were prepared using the similar synthetic methods.

Radical cation salts of **3a–3f** with various counter anions such as AuI_2^-, I_3^-, and Br^- were prepared by electrochemical crystallistallization in the presence of the corresponding tetrabutylammonium salts as supporting electrolyte. The obtained salts are typically needle-shape crystals and highly conducting along the needle-axis direction. Their conducting properties are summarized in Table I, and the temperature dependence of resistivity of (MDT-TSF)-AuI_2 is shown in Figure 2, as a representative. Note that not only these radical cation salts are highly conducting but also some of them show superconductivity. Among these superconducting radical cation salts, the salts derived from MDT-TSF (**3a**), MDT-ST (**3c**), and MDT-TS (**3d**) are isostructural to one another; their crystal structures elucidated by means of X-ray crystallographic analysis consist of uniform donor stacks and incommensurate anion lattice (Figure 3). Owing to the incommensurate structure, the donor/anion ratios of these salts are deviated from typical 2:1 (Table I). These superconductors with the unusual structural characteristics are of current

TABLE I Some Radical Cation Salts of 3a–3f

Donor	Anion	D:A[a]	σ_{rt}/S cm^{-1}[b]	Remarks	Reference
MDT-TSF (**3a**)	AuI_2	1:0.436	2000	SC[c], $T_c = 4.5$ K	[9]
MDT-TSF (**3a**)	I_3	1:0.42	1500	SC, $T_c = 4.6$ K	[22]
MDS-TSF (**3b**)	Br	2:1	200–1000	SC, $T_c = 4.0$ K	[23]
MDT-ST (**3c**)	I_3	1:0.42	600–1200	SC, $T_c = 3.8$ K	[24]
MDT-TS (**3d**)	AuI_2	1:0.441	300–600	SC, $T_c = 4.7$ K at 11.4 kbar	[25]
MDS-ST (**3e**)	AuI_2	1:0.44	2000–4000	Metallic to 1.5 K	[26]
MDS-TS (**3f**)	I_3	1:0.42	150–400	Metallic to 1.5 K	[26]

[a] Determined on the basis of XRD studies.

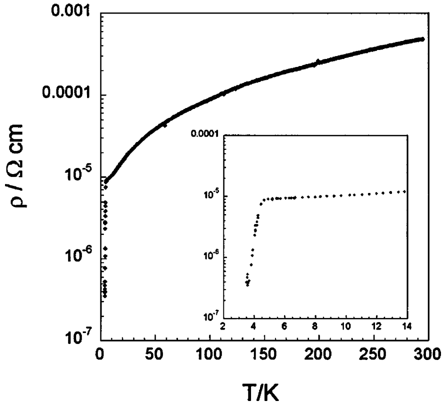
[b] Measured on a single crystal with four-probe method.

[c] SC: superconducting.

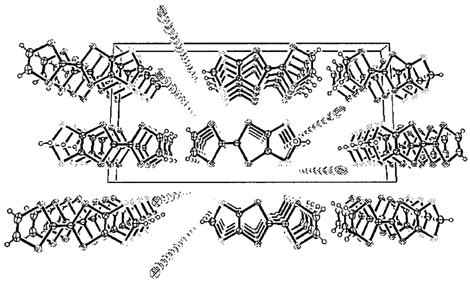
interest in the field of the solid-state physics, and detail investigations on their physical aspects are now underway.[19–21]

SELENOPHENE-BASED CONJUGATED MOLECULES AS ORGANIC SEMICONDUCTORS FOR FIELD-EFFECT-TRANSISTORS

Recent high performances of organic field-effect transistors (OFETs) have been achieved by two approaches: one is the improvement of device fabrication techniques, as represented by pentacene-based OFETs, and the other is the development of new molecular semiconductors for OFET devices.[27] Such high-performance materials mainly are comprised of thiophene-based molecules, such as oligothiophenes,[28–30] thienylene-phenylene co-oligomers,[31,32] and fused thiophene aromatics.[33–35]



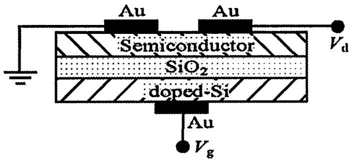
SCHEME 2 Temperature dependence of resistivity of (MDT-TSF)AuI_2.



SCHEME 3 Crystal structure of (MDT-TSF)AuI$_2$.

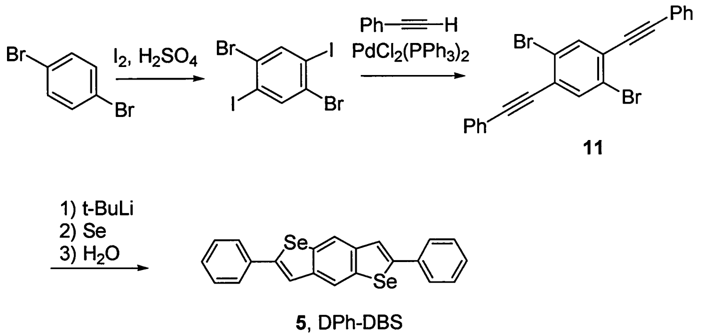
Successful improvements of solid-state properties of the aforementioned organic conductors based on selenium-containing donors has impeded us to develop the selenophene-based organic semiconductors for higher performance OFET devices.

Our first approach was to examine whether oligoselenophenes can act as semiconductors for OFET devices or not. Thus, α-quaterselenophene (**4a**) and α-quinquselenophene (**4b**) were synthesized according to the reported method and utilized in the fabrication of OFET devices, the schematic structure of which is shown in Figure 4. These devices showed typical p-type FET responses and their field-effect mobilities were 3.6×10^{-3} cm^2/Vs for **4a** and 1.9×10^{-2} cm^2/Vs for **4b**, respectively.[36] These values are almost comparable with or slightly higher than those of the thiophene counterparts, α-quaterthiphene (2.5×10^{-3} cm^2/Vs) and α-quinquthiophene (1.5×10^{-3} cm^2/Vs), respectively,[28–30] indicating that the substitution of thiophene rings by selenophene is an effective approach to develop new superior organic semiconductors. Then, we have turned our interest to selenophene-contianing acene-type compounds and have designed benzo[1,2-b:4,5-b′]diselenophene (BDS) derivative. Since the reported synthetic method for the thiophene counterpart, benzo[1,2-b:4,5-b′]dithiophene requires functionalized thiophene derivatives as key synthetic intermediates,[33–37] we have sought a new synthetic method via heterocycle formation on the central benzene ring. As a result, an efficient and general method for the synthesis of BDS



SCHEME 4 Device structure of the OFETs.

derivatives was established, and the synthesis of 2,6-diphenybenzo[1,2-b:4,5-b′]diselenophene (**5**, DPh-DBS) (Scheme 2) is shown in Scheme 2 as a representative. 1,4-Dibromobenzene was converted to 1,4-dibromo-2,5-bis(phenylethynyl)benzene (**11**) by iodization followed by the Sonogashira coupling with phenylacetylene, which was then treated with t-BuLi followed by an addition of selenium powder to give **5** in 74% isolated yield.[38] Other BDS derivatives with biphenyl-, p-hexylphenyl-, 2-naphthyl-subsistents also can be synthesized by the same method using the corresponding arylacetylenes.[39]



SCHEME 2 Synthesis of DPh-BDS (**5**).

Field-effect transistors with a top-contact geometry were fabricated by the vapor deposition technique. The device characteristics of FET with DPh-DBS are shown in Figure 5. It demonstrates a typical p-type FET response, i.e., I_{DS} scales up with increasing V_G. The field-effect mobility calculated using the I_{DS} in the saturation regions is

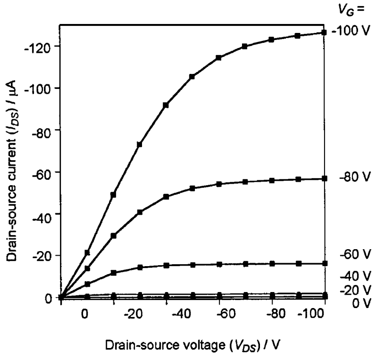


FIGURE 5 Drain-source current (I_{DS}) versus drain-source voltage (V_{DS}) characteristic for **5**.

0.17 cm^2/Vs, and the on/off ratio of the I_{DS} between V_G of 0 and -100 V is greater than 10^5.[37] This FET performance is among the best class of OFETs based on thin films of organic materials, indicating that the selenophene-contianing acene-type compounds will be promising for high-performance semiconductors for OFET devices.

CONCLUDING REMARKS

This article has described our recent results on the selenium-containing π-conjugated systems for the development of organic superconductors and semiconductors for OFET devices. Our approach is based on the synthetic studies aiming to establish a widely applicable synthetic method for the selenium-containing compounds potentially interesting. The present results clearly show that the new synthetic methods for selenium-containing materials contribute to the development of superior organic electronic materials.

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