Highlight Review

Development of New Semiconducting Materials for Durable High-performance Air-stable Organic Field-effect Transistors

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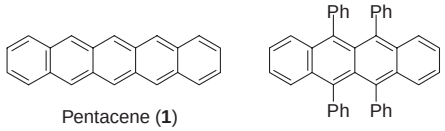
Abstract

New thiophene- and selenophene-fused aromatic compounds were successfully developed as high-performance semiconducting materials for organic field-effect transistors (OFETs). Among them, the most advanced compounds designed on consideration of structure–function relationship showed durable air-stable FET performance. This article highlights the research strategy and development of these superior compounds as well as the molecular factors for the improvement of mobility, sensitivity, and stability, which are very informative for the design of practical semiconductors.

♦ Introduction

Organic field-effect transistors (OFETs) have attracted much attention in the context of inexpensive, flexible, large-area electronics devices such as bendable displays, electronic paper, smart cards, ID tags, and sensors.[1] To realize their commercial application, however, OFETs require further improvements in device performance to ensure that they at least match the performance of conventional amorphous silicon-based transistors. Improvements in OFET performance are currently being driven by two different approaches: the optimization of device structures and the development of new organic semiconductors. In terms of device structure, it is noteworthy that device optimization for pentacene (**1**) (Chart 1) markedly enhanced the initially reported hole mobility[2] of 0.002 $cm^2 V^{-1} s^{-1}$ to the most recently obtained value[3] of 3.0 $cm^2 V^{-1} s^{-1}$, the highest among thin film organic semiconducting materials. Furthermore, a state-of-the-art single crystal device using rubrene (**2**) set the mobility record for OFETs (15–20 $cm^2 V^{-1} s^{-1}$);[4] however, such device optimization on the basis of known semiconducting materials appears to be limited as far as improvements to mobility are concerned. In contrast, the development of new organic semiconductors has the potential to lead to a breakthrough in OFET development in all respects of carrier mobility, sensitivity, and stability. For this reason, new organic semiconductors are currently being intensively studied, resulting in the development of a growing number of high-performance semiconducting materials with higher mobilities than that of amorphous silicon (0.1 $cm^2 V^{-1} s^{-1}$); however, almost all organic semiconductors share the severe drawback of being unstable in device operation, resulting in poor reliability and durability. A major challenge in OFET research is therefore the development of practical OFET materials that ensure not only high performance but also high stability in the operational environment. This is a formidable task as the development of such OFET materials requires not only the design of air-, photo-, and thermostable semiconducting molecules but also the precise control of molecular ordering in the thin film phase. For the time being, however, there are no definite guidelines for "molecular engineering designs" that are capable of forming interactive networks advantageous for charge migration. As part of our strong interest in modern molecular electronics materials, our group has recently been engaged in the design and synthesis of new organic semiconductors. Among the newly developed thiophene- and selenophene-fused compounds, we have found air-stable semiconductors that provide high performance during continuous FET operation and after long periods of storage. In this paper, we describe our research strategy and progress in developing these practical OFET materials.



Pentacene (**1**) Rubrene (**2**)

Chart 1.

♦ Strategy for Development of High-performance OFET Materials

Redox-active π-conjugated compounds generally qualify as candidates for organic semiconductors; however, strong electron donors or acceptors that are commonly used for conductive molecular complexes are unfavorable for use as OFET materials because the devices that use these compounds suffer from poor FET performance due to low on/off sensitivity and environmental instability.[5] In fact, good p-channel OFET materials have been found among weak electron-donating compounds. The representative materials are polyacenes such as pentacene and rubrene with extraordinarily high mobilities.[6] However, such polyacenes have the serious disadvantage of readily undergoing air- and/or photooxidation, leading to degraded OFET perform-

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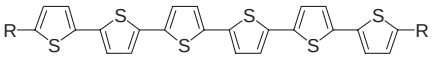
ance under ambient conditions. Recent intensive research in the development of OFET materials has been directed toward weakly electron-donating thiophene-containing aromatic compounds such as oligothiophenes, polythiophenes, thiophene-arene co-oligomers, thiophene-vinylene co-oligomers, and thiophene-fused aromatics, which are thermally and photochemically more stable than polyacenes. Among them, the most well studied are small oligothiophenes represented by α-sexithiophene (**3**)[7] and its α,ω-dihexyl derivative **4** (Chart 2),[8] which give high-quality ordered films by vapor deposition and hence exhibit high FET mobilities of up to 10^{-1} to 10^{-2} cm^2 V^{-1} s^{-1}.

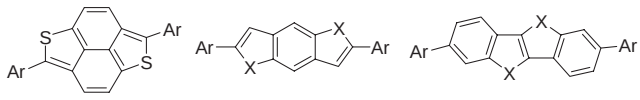


3 R = H
4 R = C_6H_{13}

Chart 2.

The high mobilities of OFET materials are closely associated with intermolecular π-electronic interactions in the macroscopically ordered film phase.[9] The limited mobilities of α-sexithiophenes compared with pentacene and rubrene can thus be speculated to reflect insufficient π-interactions in the molecular assembly. The chain extension of oligothiophenes might increase intermolecular π-interactions, but the molecules then become non-volatile and insoluble. Long oligothiophenes solubilized by alkylation at the β-positions like poly(3-alkylthiophene)s serve as solution-processsible OFET materials.[10] Such solution-processing films are well suited for device fabrication with easy patterning at low cost and on large areas;[11] however, they are generally inferior in film quality and hence in FET performance compared with vapor-deposited film. To ensure compatibility between the increasing π-interaction and the vapor deposition of thiophene-containing compounds, we focused on thiophene-fused aromatic systems; we took this approach because appropriately expanded systems have the possibility of forming a strongly π-interactive molecular assembly. Some thiophene-fused aromatics **5**–**10** (Chart 3) show good FET performance, but their mobilities have yet to match those of pentacene and rubrene.[12]

Our strategy for developing practical OFET materials is first to search novel thiophene-fused aromatics for prototypical high-performance p-channel semiconducting systems; second, to find air-stable systems among them; and third, to extend the scope of research into n-channel semiconducting systems. Our final goal is to develop durable air-stable organic semiconducting materials for practical applications. In the search for potential thiophene-fused aromatics, we found that three systems **11**–**13** (Chart 4) are prototypical architectures for high-performance semiconductors. The first system **11** consists of the naphtho[1,8-*bc*:5,4-*b*′*c*′]dithiophene core, which was found among electron donors developed for molecular complexes. The second system **12** contains the benzo[1,2-*b*:4,5-*b*′]dichalcogenophene core, which was developed as a prototype for readily accessible air-stable semiconductors. The last system **13** is based on the [1]benzochalcogenopheno[3,2-*b*][1]benzochalcogenophene core, which was developed as a prototype for durable air-stable semiconductors. In systems **12** and **13**, the FET performance of the thiophene- and selenophene-fused counterparts was compared. All of these systems are modified with aryl substitution at the terminals because of the formation of good films. In the designs of these systems, we have taken into account many molecular factors such as the expanded π-framework, the chalcogen effect, the Frontier MO energy level, high stability, and ready accessibility, all of which affect the structure–FET property relationship. Here, we outline the FET characteristics of the three types of semiconductors and discuss useful molecular factors in designing practical OFET materials with high charge-carrier mobility and high operational stability.

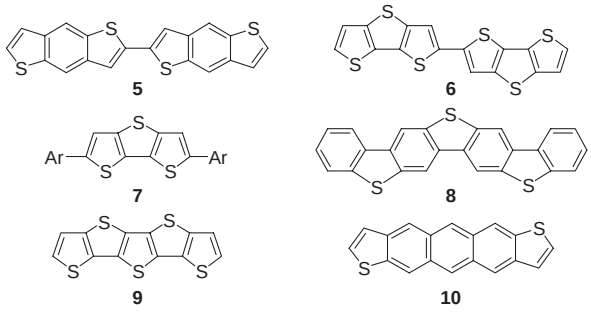


11 **12** X = S, Se **13** X = S, Se

Chart 4.

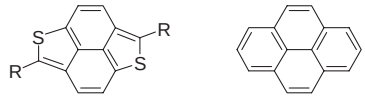
♦ *Diarylnaphthodithiophenes as High-performance p-Channel Semiconductors*

As mentioned above in our strategy for the development of high-performance OFET materials, we believe that appropriately expanded thiophene-fused aromatics are promising molecular systems. In exploring new molecular conductors, we previously developed a variety of redox-active thiophene-fused aromatics[13] including naphtho[1,8-*bc*:5,4-*b*′*c*′]dithiophene (**14**), which has an intriguing π-structure.[14] This material is formally isoelectronic with pyrene (**20**), but replacement of the two benzene rings of pyrene with thiophenes greatly perturbs the Kekulé resonance structure (Chart 5). In fact, the Frontier MO energies of the naphthodithiophene **14** (HOMO −4.98 eV and LUMO −1.87 eV) on DFT calculation at the B3LYP–6-31G(d) level using the PCGAMESS program[15] are considerably different from those of pyrene (HOMO −5.34 eV and LUMO −1.48 eV). Consistent with the elevation of the HOMO energy level,



5 **6** **7** **8** **9** **10**

Chart 3.



14 R = H
15 R = Ph
16 R = 2-naphthyl
17 R = 4-biphenylyl
18 2-thienyl
19 2,2'-bithiophen-5-yl

20

Chart 5.

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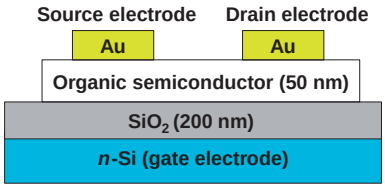


Figure 1. Schematic drawing of the top-contact OFET device structure.

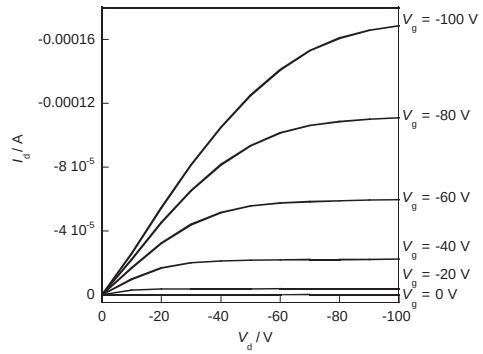


Figure 2. FET characteristics of 2,6-di(2-naphthyl)naphtho-[1,8-*bc*:5,4-*b*′*c*′]dithiophene (**16**).

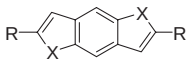
it has a greater electron-donating ability than pyrene and forms highly conductive molecular complexes with iodine or DDQ.

In the search for new OFET materials, we first focused on the naphthodithiophene system, as the Frontier MO energies of **14** are similar to those of α-sexithiophene (HOMO -4.99 eV and LUMO -1.99 eV); however, the parent compound **14** was too crystallizable to form a homogeneous thin film for device fabrication. As an alternative, we examined the phenyl, 2-naphthyl, 4-biphenylyl, 2-thienyl, and 2,2′-bithiophen-5-yl derivatives **15**–**19**, which gave thin films using the vapor-deposition technique.[16]

Figure 1 shows a schematic drawing of OFET devices fabricated using these films in a top-contact configuration. All of the devices showed typical p-channel FET performance in an inert atmosphere. Figure 2 shows drain–source currents versus drain–source voltages at various gate voltages observed for the device using **16**. The hole mobilities of **15**–**19** in the saturation regime are relatively high in the range of 10^{-1} to 10^{-3} cm^2 V^{-1} s^{-1}, and are dependent on the aryl groups as well as the Si/SiO$_2$ substrate temperatures during vapor deposition. In particular, when fabricated at the substrate temperature of 140 °C, the device based on **16** shows a high mobility of 0.11 cm^2 V^{-1} s^{-1} and a high on/off ratio of 10^5, which are among the top class of FET performance among thin film organic semiconductors.

♦ *Diarylbenzodichalcogenophenes as Air-stable, High-performance p-Channel Semiconductors*

Although they are high-performance p-channel semiconductors, 2,6-diarylnaphtho[1,8-*bc*:5,4-*b*′*c*′]dithiophenes **15**–**19** have a major drawback in that they require an elaborate multi-step synthesis from commercially available chemicals; this inaccessibility is fatal for utilization as electronics materials. Another

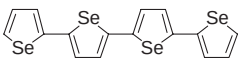


21 X = S, R = Ph
22 X = Se, R = Ph
23 X = Se, R = 2-naphthyl
24 X = Se, R = 4-biphenylyl

Chart 6.

drawback is that the devices do not work in air. These results directed our attention toward a more realistic thiophene-fused aromatic system for OFET materials. The new compound that we designed with ready access and air stability in mind is 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]dithiophene (**21**) (Chart 6).[17] The core skeleton is comprised of three fused rings; accordingly, the synthetic route is simpler than that of the diarylnaphthodithiophene system with four fused rings. However, the smaller π-framework might lack sufficient intermolecular π-interaction. To compensate, we intended to incorporate highly polarizable selenium atoms rather than sulfur atoms. In the molecular modification of tetrathiafulvalene, replacement of the skeletal sulfur atoms with selenium led to the discovery of highly conductive organic (super)conductors.[18] A similar heavy chalcogen effect that enhances intermolecular π-interaction is expected for 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]diselenophene (**22**).

With regard to the heavy chalcogen effect expected for the benzo[1,2-*b*:4,5-*b*′]diselenophene system, it is worth mentioning that the chalcogen effect of α-oligoselenophenes on FET performance is only marginal. OFETs using α-quaterselenophene (**25**) as an active semiconducting layer showed a mobility of 0.0036 cm^2 V^{-1} s^{-1}, which is similar to that of the α-quaterthiophene counterpart.[19] This is explained in terms of the specific electronic structures of α-oligochalcogenophenes.



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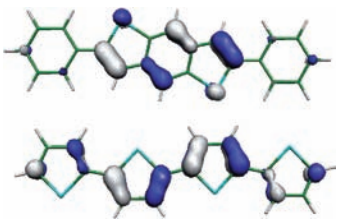


Figure 3. Atomic coefficients in the HOMOs of 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]diselenophene (**22**) (upper) and α-quaterselenophene (**25**) (lower).

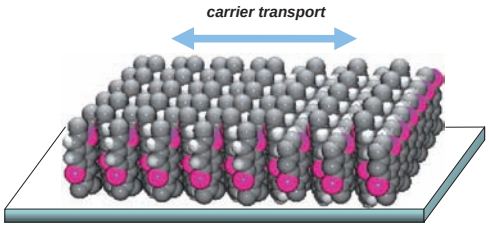
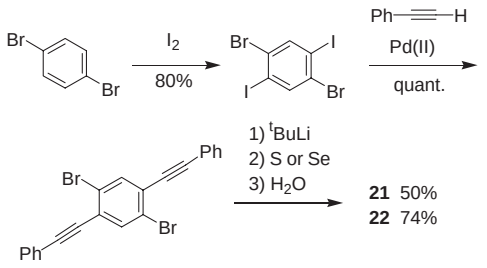


Figure 4. Schematic illustration of the molecular arrangement of 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]diselenophene (**22**) on the substrate.



Scheme 1. Synthesis of 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophenes **21** and **22**.

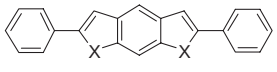
In the variable range hopping model, it is accepted that charge migration of conducting molecules takes place via the overlapping of Frontier MOs. As depicted in Figure 3 (lower drawing), the HOMO orbital of α-quaterselenophene has almost no atomic coefficients on the chalcogen atoms, meaning that chalcogen interactions do not contribute to charge migration. In contrast, the HOMO orbital of **22** has large coefficients on the selenium atoms (Figure 3, upper drawing). Accordingly, in this system, the polarizable selenium atoms have the potential to enhance intermolecular interactions for charge migration.

Compounds **21** and **22** were unknown at the time that we studied them. Scheme 1 shows a ready synthetic method of **21** and **22** that was successfully developed by our group.[17,20] This three-step synthetic method is quite straightforward and has a high overall yield; therefore, it is attractive for materials synthesis. The last step involves a unique heterocyclization reaction to give either **21** or **22** depending on the sulfur and selenium reagents employed in the process. In the second step, the reaction with 4-biphenylylacetylene or 2-naphthylacetylene instead of phenylacetylene enables the synthesis of the biphenylyl and naphthyl derivatives **23** and **24**.

All of the devices using 2,6-diarylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophenes showed good p-channel FET performance under atmospheric conditions. The hole mobilities of **21** and **22** are 0.081 and 0.17 $cm^2 V^{-1} s^{-1}$, respectively. The fact that the mobility of the selenophene counterpart **22** is twice as high as that of **21** supports the heavy chalcogen effect. The biphenylyl derivative **23** and the naphthyl derivative **24** also showed high mobilities of 0.24 and 0.05 $cm^2 V^{-1} s^{-1}$, respectively. In addition, when measured by the devices using single crystals, the mobilities of **21** and **22** were enhanced to 0.4 and 1.5 $cm^2 V^{-1} s^{-1}$, respectively.[21]

X-ray crystallographic analysis of **22** revealed that the molecules are completely planar and, as with pentacene and α-sexithiophene, packed in a herringbone manner with extensive edge-to-face interactions. In addition, X-ray diffraction analysis of the thin film revealed that the molecules stand nearly upright on the substrate and assemble in a highly ordered arrangement to closely interact with one another, being responsible for the high carrier transport (Figure 4).

Compared with the diphenylbenzodichalcogenophenes **21** and **22**, structural isomers **26** and **27** (Chart 7) showed low hole



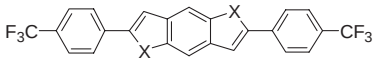
26 X = S
27 X = Se

Chart 7.

mobilities of 0.003 and 0.02 $cm^2 V^{-1} s^{-1}$, respectively, indicating the importance of structural symmetry for "molecular engineering design."[22]

♦ *Bis(trifluoromethylphenyl)benzodichalcogenophenes as High-performance n-Channel Semiconductors*

In contrast to an increasing number of p-channel organic semiconductors, good n-channel examples are limited to specific electron acceptors such as fullerenes, naphthalene- and perylenetetracarboxylimides, dicyanomethylene-substituted quinoidal oligothiophenes, tetracyanonaphthoquinodimethanes, and perfluoroaromatics.[23] The poor chemistry of n-channel organic semiconductors is ascribable to a mismatch between the LUMO levels of organic molecules and the work functions of the gold metal generally used for the source and drain electrodes of OFET devices. Recent developments of n-channel semiconductors have been conveniently promoted by introducing strong electron-withdrawing groups into the π-frameworks of relatively readily accessible high-performance p-channel semiconductors.[24] In connection with the superior p-channel FET characteristic of the 2,6-diarylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophene system **12**, we intended to develop novel n-channel semiconductors by introducing a strong electron-withdrawing group into the attached aryl moieties. The intended conversion from p- to n-channel OFET materials in this system was achieved for 2,6-bis(4-trifluoromethylpheny)benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes **28** and **29** (Chart 8).[25]



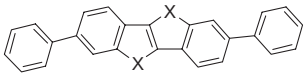
28 X = S
29 X = Se

Chart 8.

The 4-trifluoromethylphenyl derivatives **28** and **29** showed typical n-channel FET characteristics with electron mobilities of 0.0048 and 0.040 $cm^2 V^{-1} s^{-1}$, respectively, when measured with gold electrodes under an inert atmosphere. The observation of high threshold voltages (60–70 V) suggested a large injection barrier between the gold electrodes and the organic layer. Consistent with this speculation, the threshold voltage was effectively reduced by 20–30 V compared with that of gold electrodes, when measured using silver electrodes with a lower work function. Interestingly, the mobilities were also markedly enhanced to 0.044 $cm^2 V^{-1} s^{-1}$ for **28** and 0.10 $cm^2 V^{-1} s^{-1}$ for **29**; the on/off ratio was increased to 10^5. These FET performances are among the top level of those reported for n-channel OFET materials.

♦ *Diphenylbenzochalcogenophenobenzochalcogenophenes as Durable High-performance Semiconductors*

The development of stable organic semiconductors that enable the operation of OFETs under ambient conditions has become an increasingly important task.[26,27] Most of p-channel organic semiconductors have relatively high HOMO energy levels and small HOMO–LUMO energy gaps. The instability of OFETs is thus ascribable to the decomposition of organic



30 X = S
31 X = Se

Chart 9.

Table 1. HOMO and LUMO energy levels[a] and HOMO–LUMO gaps of organic semiconductors, and their device stability

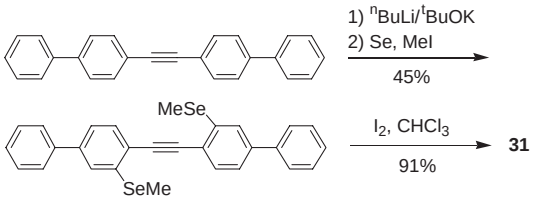
Comp.	HOMO/eV	LUMO/eV	Gap/eV	Device stability
1	−4.56	−2.39	2.17	air-unstable
3	−4.99	−1.99	3.01	air-unstable
15	−4.72	−2.13	2.59	air-unstable
21	−5.24	−1.71	3.53	air-stable
22	−5.21	−1.73	3.48	air-stable
25	−4.93	−2.05	2.88	air-unstable
30	−5.41	−1.52	3.89	air-stable, durable
31	−5.38	−1.52	3.86	air-stable, durable

[a]DFT calculation at the B3LYP–6-31G(d) level.

semiconductors due to air oxidation and photolysis. The presence of decomposition impurities in thin film leads to a decrease in the on-current due to carrier trap and an increase in the off-current due to unintended doping, resulting in low mobility and a low current on/off ratio for the OFET. It has recently been proposed that durable p-channel organic semiconductors have low HOMO energy levels and large HOMO–LUMO energy gaps.[27] Table 1 compares the Frontier MO levels of typical organic semiconductors discussed in this article. The air stability of the devices based on 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]-dichalcogenophenes **21** and **22** can be explained by their lower HOMO energy levels and larger HOMO–LUMO gaps relative to pentacene (**1**), α-sexithiophene (**3**), 2,6-diphenylnaphtho-[1,8-*bc*:5,4-*b*′*c*′]dithiophene (**15**), and α-quaterselenophene (**25**), all of which are air-unstable. With the aim of developing additional durable air-stable semiconductors, we next designed the diarylbenzochalcogenophenobenzochalcogenophene system **13**, taking into account its structural similarity to the air-stable diarylbenzodichalcogenophene system **12**. MO calculations indicated that 2,7-diphenyl[1]benzothieno[3,2-*b*][1]benzothiophene (**30**)[28] and the selenium counterpart **31**[29] (Chart 9) have lower HOMO energy levels and larger HOMO–LUMO gaps than 2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]dichalcogenophenes **21** and **22**.

Although the synthesis of **30** required multistep reactions from commercially available disodium 4,4′-dinitrostilbene-2,2′-disulfonate, we developed a relatively straightforward synthetic route for the selenium counterpart **31** by utilizing unique selenocyclization, as shown in Scheme 2.

OFET devices fabricated using thin films of **30** and **31** deposited on bare Si/SiO_2 substrate showed high mobilities of 0.26 and 0.31 $cm^2 V^{-1} s^{-1}$, respectively, together with a high on/off of $>10^6$ under atmospheric conditions. There are no virtual differences between the FET performances of these two compounds, although the HOMO orbital of **31** has large coefficients on the chalcogen atoms. The expanded π-framework of this system no longer requires the heavy chalcogen effect for enhanced intermolecular interaction. It is notable that the device of **30** fabricated on the Si/SiO_2 substrate surface-treated with octyltrichlorosilane-SAM showed a yet higher mobility of



Scheme 2. Synthesis of 2,7-diphenyl[1]benzoselenopheno-[3,2-*b*][1]benzoselenophene (**31**).

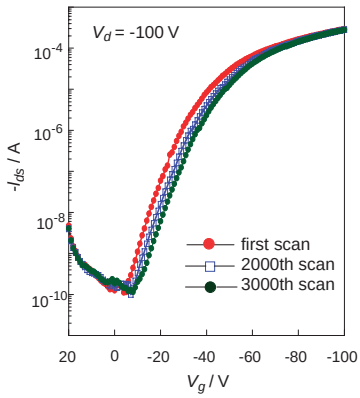
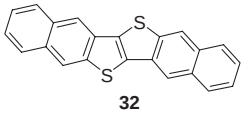


Figure 5. FET characteristics of 2,7-diphenyl[1]benzoselenopheno[3,2-*b*][1]benzoselenophene (**31**) under continuous operation.

2.0 $cm^2 V^{-1} s^{-1}$. In the stability tests, both devices of **30** and **31** were highly durable, undergoing no significant deterioration under long-term continuous operation and during long-term storage for at least 12 months under ambient laboratory conditions. Figure 5 demonstrates the durable FET characteristics of **31**. Both performance and stability meet the criteria for practical p-channel OFET materials.

The superior FET performances of **30** and **31** as durable high-performance semiconducting materials exceeded our expectations. The expansion of these π-frameworks has the potential to provide even more high-performance organic semiconductors. A compound that we very recently designed with this idea in mind is dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (**32**) (Chart 10) with six fused aromatic rings.[30] The calculated HOMO and LUMO levels for this compound are 5.19 and 1.81 eV, respectively, below the vacuum level. In a preliminary examination, the device fabricated with **32** operated in air and showed a very high hole mobility of 2.9 $cm^2 V^{-1} s^{-1}$, close to the record level of thin film pentacene; the on/off ratio of 10^7 is also excellent.



32

Chart 10.

♦ Summary and Future Outlook

Precise control of molecular ordering with strong π-interactions in the thin-film phase is crucial for high FET performance. In addition, practical OFET materials must be air-, photo-, and

thermostable in the operational environments. The present article outlined the research strategy and the development of three thiophene(or selenophene)-fused high-performance semiconducting systems; this provides a useful guideline in designing practical OFET materials. The planar, straight π-frameworks are evidently helpful in forming a highly ordered structure in the film phase where the molecules stand nearly upright on the substrate and assemble in such a way as to closely interact with one another. The expansion of the π-frameworks and the incorporation of selenophene rings into the π-frameworks serve to strengthen the π-interactions. Molecular designs based on lower HOMO energy levels and larger HOMO–LUMO gaps are valid for durable air-stable p-channel semiconducting materials. Durable high-performance air-stable n-channel semiconducting materials remain attractive targets in the research of OFETs.[31] Introduction of appropriate electron-accepting groups at the terminals of the present thiophene-fused systems gives a useful approach to n-channel OFET materials. The availability of both durable high-performance p- and n-channel semiconducting materials and durable high-performance ambipolar semiconducting materials should promote the development of effective CMOS-like OFET devices.

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