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Isomerically Pure Anthra[2,3-*b*:6,7-*b*′]-difuran (*anti*-ADF), -dithiophene (*anti*-ADT), and -diselenophene (*anti*-ADS): Selective Synthesis, Electronic Structures, and Application to Organic Field-Effect Transistors

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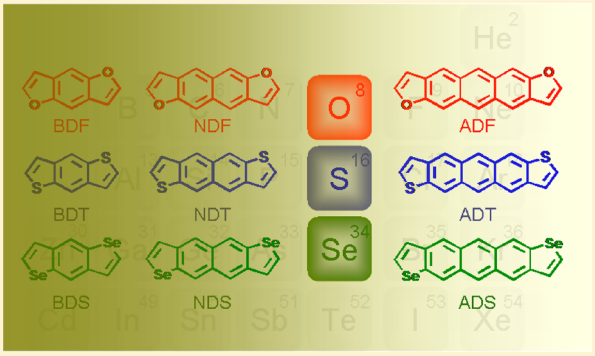
Supporting Information

ABSTRACT: A new straightforward synthesis of isomerically pure anthra[2,3-*b*:6,7-*b*′] -difuran (*anti*-ADF), -dithiophene (*anti*-ADT), and -diselenophene (*anti*-ADS) from readily available 2,6-dimethoxyanthracene is described. The present successful synthesis makes it possible to overview the linear-shaped *anti*-acenedichalcogenophene compounds, that is, benzo[1,2-*b*:4,5-*b*′]-, naphtho[2,3-*b*:6,7-*b*′]-, and anthra[2,3-*b*:6,7-*b*′]- difuran, -dithiophene, and -diselenophene. By comparing their electrochemical and photochemical properties, the electronic structures of acenedichalcogenophenes can be expressed as the outcome of balance between the central acene core and the outermost chalcogenophene rings. Among isomerically pure parent *anti*-anthradichalcogenophenes, *anti*-ADT and *anti*-ADS can afford crystalline thin films by vapor deposition, which acted as active layer in organic field-effect transistors with mobility as high as 0.3 $cm^2 V^{-1} s^{-1}$ for ADT and 0.7 $cm^2 V^{-1} s^{-1}$ for ADS. The mobility of isomerically pure *anti*-ADT is higher by several times than those reported for isomercally mixed ADT, implying that the isomeric purity could be beneficial for realizing the better FET mobility. We also tested the diphenyl derivatives of *anti*-ADF, -ADT, and -ADS as the active material for OFET devices, which showed high mobility of up to 1.3 $cm^2 V^{-1} s^{-1}$.



INRODUCTION

Acenedithiophenes (AcDTs), where two thiophene rings fused at both ends of acene cores, have been the representative thienoacene structures and widely utilized as key building blocks in the development of superior organic semiconductors[1] applicable to organic electronic devices such as organic field-effect transistors (OFETs)[2−4] and organic photovoltaics (OPVs).[5−8] Large numbers of materials based on benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT),[2,5] isomeric naphthodithiophenes (NDTs),[3,6] and anthra[2,3-*b*:6,7(7,6)-*b*′]dithiophene (ADT)[4,7,8] have been developed and enriched the material diversity of this class, which has indeed contributed to recent progress in the field of π-functional materials and organic electronics (Chart 1).

From the viewpoint of synthetic organic chemistry, there had remained several challenges in the acenedithiophene chemistry, one of which is the synthesis of linear-shaped NDTs and the other is a selective synthesis of isomerically pure *syn*- and *anti*-ADT. The former has been addressed recently by two research groups developing the new methods for the efficient synthesis of NDTs.[3,6] For the latter issue, on the other hand, Anthony and co-workers have successfully isolated pure *syn*- and *anti*-ADT derivatives with amide substituents at the thiophene π-positions by fractional recrystallization from the *syn* and *anti* isomeric mixture.[8] Furthermore, Geerts and co-workers have recently reported the first selective synthesis of isomerically pure *anti*-ADTs with π-alkyl substitutents via a multistep synthetic protocol.[9] Also, the isomerically pure *syn*-ADT derivatives[10] and its related molecules, anthra[2,3-*b*:7,6-*b*′]bis[1]benzothiophenes (*syn*-ABBTs), have been successfully synthesized.[11] In addition to these recent synthetic developments, Mamada and co-workers have just published synthesis, characterization, and FET characteristics of isomerically pure *syn*- and *anti*-dimethyl-ADTs.[12] However, the selective synthesis of isomerically pure parent *anti*-ADT, one of the most basic compounds in this class, has remain unattained.

We were interested in the synthesis and application of benzo[*b*]thiophene-based π-extended materials and developed several practical methods for the synthesis of compounds of this class.[13] Among the methods, the thiophene-annulation reaction of *o*-halogen substituted ethynylbenzene substructure effected by sodium sulfide is a very useful reaction that allows efficient and scalable synthesis of not only benzo[*b*]thiophenes[13h] and

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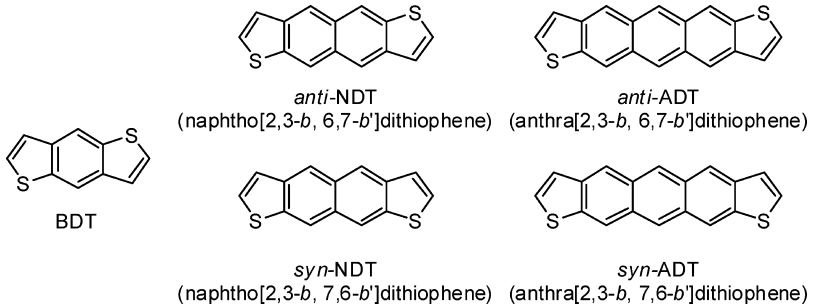
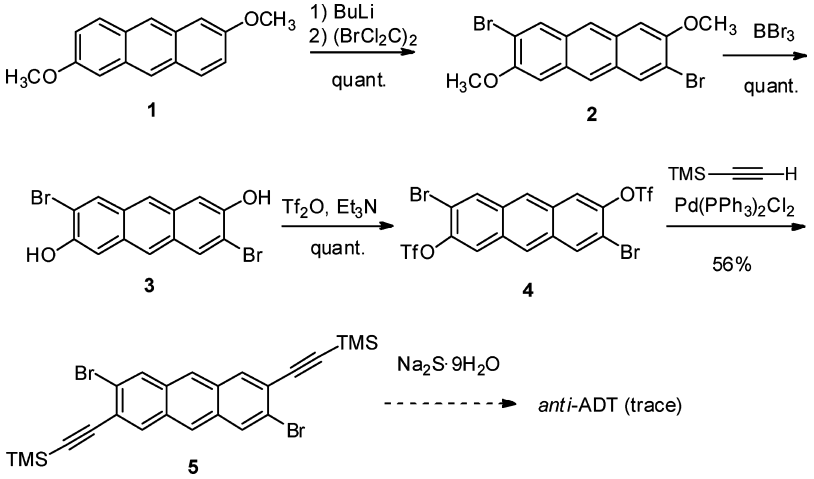
Chart 1. Molecular Structures of Representative Linear-shaped Acenedithiophenes



Scheme 1. Attempted Synthesis of *anti*-ADT from 2,6-Dimethoxyanthracene (1)



anthra[2,3-*b*]thiophene[13l] (one-fold cyclization) but also BDTs[13h] and NDTs[3a,b] (2-fold cyclization), and furthermore, benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophenes (BTTs, 3-fold cyclization).[13h] We therefore attempted to employ this reaction for the synthesis of *anti*-ADT, starting from 2,6-dimethoxyanthracene,[14] where 2- and 6- methoxyl groups can act as a strong *o*-directing group in lithiation reaction to give the corresponding 3,7-dilithiated intermediate.[13k,15] Although, as will be discussed later, the first attempt to synthesize *anti*-ADT using the thiophene-annulation reaction failed, the selective functionalization on 3- and 7-positions on 2,6-dimethoxyanthracene turned out to pave the way to the efficient synthesis of not just isomerically pure parent *anti*-ADT but also anthra[2,3-*b*:6,7-*b*′]-difuran (*anti*-ADF) and -diselenophene (*anti*-ADS). The successful synthesis also provides an opportunity to compare a range of linear-shaped acenedichalcogenophenes with benzene, naphthalene, and anthracene as the central acene and furan, thiophene, and selenophene as the outermost chalcogenophene rings. We here first report the synthesis and characterization of *anti*-anthradichalcogenophenes and then discuss their electronic properties in comparison with their lower homologues, benzo[1,2-*b*:4,5-*b*′]- and naphtho[2,3-*b*:6,7-*b*′]- dichalcogenophenes. Then, the parent and diphenyl derivatives of these *anti*-anthradichalcogenophenes were examined as the active layer in OFETs, showing mobility of up to 1.3 $cm^2\ V^{-1}\ s^{-1}$.

RESULTS AND DISCUSSION

Synthesis and Characterizations. As depicted in Scheme 1, lithiation of 2,6-dimethoxyanthracene (**1**) with excess BuLi followed by the reaction with dibromotetrachloroethane *selectively* gave 3,7-dibromo-2,6-dimethoxyanthracene (**2**) in a quantitative yield. Demethylation with BBr_3 gave the corresponding dihydroxyanthracene (**3**) quantitatively, which was then converted into the corresponding triflate (**4**). The chemoselective Sonogashira coupling reaction with trimethylsilyl acetylene at the triflate site gave the potential precursor (**5**) for parent *anti*-ADT in 56% isolated yield. The thiophene annulation reaction promoted by the sodium sulfide reagent, however, gave a complex mixture as a black solid, which afforded a trace amount of ADT after gradient sublimation in vacuum. The failure in the synthesis of ADT could be attributed to undesired reactions of the reagent with the substrate (**5**) at the 9- and 10-positions of anthracene or with in situ generated ADT at the most reactive 5- and 11-positions under the harsh reaction conditions, that is, high temperature and the highly reactive and basic sodium sulfide reagent. Considering the successful synthesis of anthra[2,3-*b*]thiophene from 2-bromo-3-[2-(trimethylsilyl)ethyn-1-yl]anthracene with sodium sulfide,[13l] it is most likely that the reaction itself afforded ADT, but it reacted with the reagent to result in a complex mixture. In fact, we confirmed that treatment of *anti*-ADT, synthesized by another route (vide infra), under the same reaction condition forms a similar mixture. It is thus concluded that this is the limitation of the sodium sulfide-induced thiophene annulation reaction in the synthesis of π-extended acenedithiophene compounds.

On the other hand, 2,6-dibromo-3,7-dihydroxyanthracene (**3**) seemed to be an ideal intermediate for the synthesis of isomerically pure anthra[2,3-*b*:6,7-*b*′]difuran (*anti*-ADF) and its derivatives, since the corresponding naphthalene analogue, 2,6-dibromo-3,7-dihydroxynaphthalene can be readily converted into naphtho[2,3-*b*:6,7-*b*′]difuran (*anti*-NDF) deriva-

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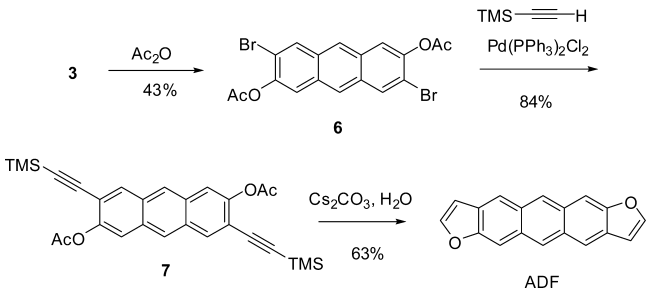
tives.[16] As in the synthesis of *anti*-NDFs, the bromine atoms were first replaced with acetylene moieties by the Sonogashira reaction after acetylation on the hydroxyl groups. Then, the subsequent base-promoted furan formation[17] at the acetyl-protected *o*-ethynylphenol substructures readily gave *anti*-ADF in acceptable yield (Scheme 2). Parent *anti*-ADF after

Scheme 2. Synthesis of *anti*-ADF from 2,6-Dibromo-3,7-dihydroxyanthracene (3)



purification by repetitive sublimations was well characterized by spectroscopic and combustion analysis (see Experimental section), and the selective formation of *anti*-ADF core was confirmed by ^{13}C NMR spectra, in which nine peaks assignable to aromatic carbons were clearly observed, indicating that the product has the centrosymmetric C_{2h} structure, not the C_{2v} (*syn*-ADF) structure consisting of 10 nonequivalent carbons or their mixture (see Supporting Information).

Going back to the synthesis of *anti*-ADT, it is important to circumvent the problems associated with sodium sulfide-induced thiophene annulation reaction, that is, high temperature and the highly reactive reagent. We thus examined an alternative route to ADT by employing the Larock thiophene annulation reaction on the *o*-ethynyl-methylmercaptobenzene substructure (Scheme 3).[18] Dilithiated 2,6-dimethoxyanthracene was first reacted with dimethyldisulfide to give 2,6-dimethoxy-3,7-bis(methylthio)anthracene (**8**) in quantitative isolated yield. After selective demethylation of the methoxy groups and subsequent triflation to give **10**, the Sonogashira coupling reaction with trimethylsilylacetylene afforded the corresponding di(ethynyl) derivative (**11**) in an excellent yield, which was then treated with iodine in dichloromethane at r.t. to give 2,8-bis(trimethylsilyl)-3,9-diiodo-ADT (**12**) in a good yield. The structure of **12** was determined by spectroscopic analyses, among which ^{13}C NMR, in particular, gave the vital spectroscopic evidence for the selective formation of *anti*-ADT substructure as in the case of ADF (see Supporting Information). Furthermore, single crystal X-ray analysis of **12** gave the concrete structural determination of the *anti*-ADT framework (Figure 1). **12** was then proven to be the direct

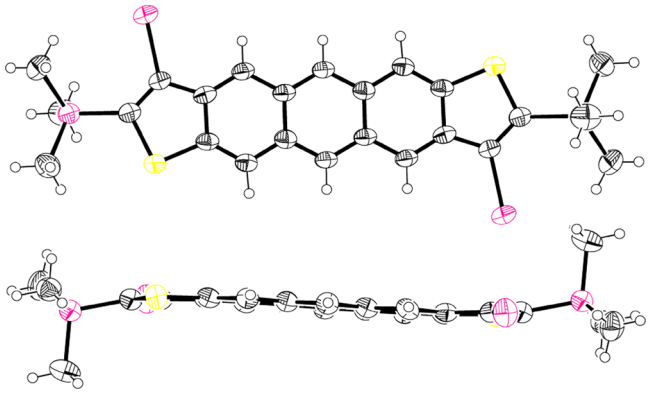
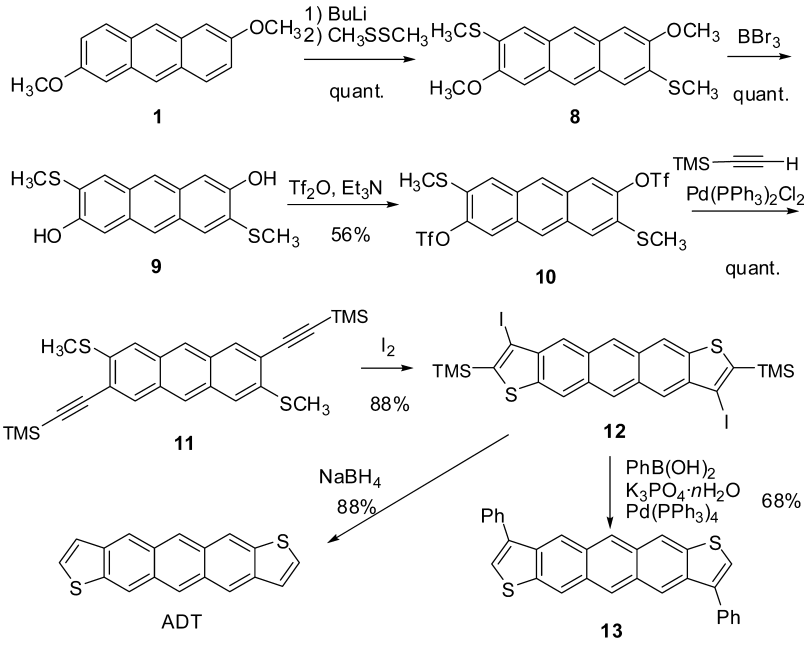


Figure 1. Single crystal X-ray structural analysis of **12** clearly shows the *anti*-ADT substructure.

precursor for parent *anti*-ADT via a hydride-promoted reductive desilylation/deiodonation (Scheme 3). In addition, the iodine atoms in **12** can be useful handles for functionalization; for example, the Suzuki-Miyaura coupling reaction between **12** and phenyl boronic acid gave the corresponding 3,9-diphenyl-ADT (**13**) in a moderate yield.[19]

Scheme 3. Synthesis of *anti*-ADT via 2,8-Substituted-3,9-diiodo-*anti*-ADT (12)



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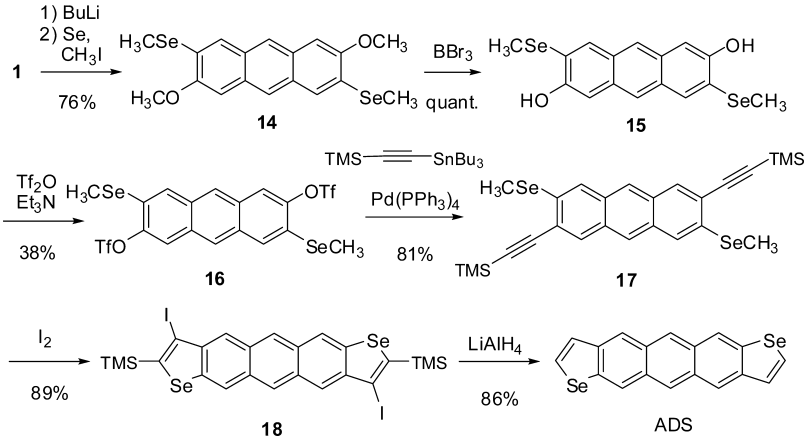
Scheme 4. Synthesis of *anti*-ADS



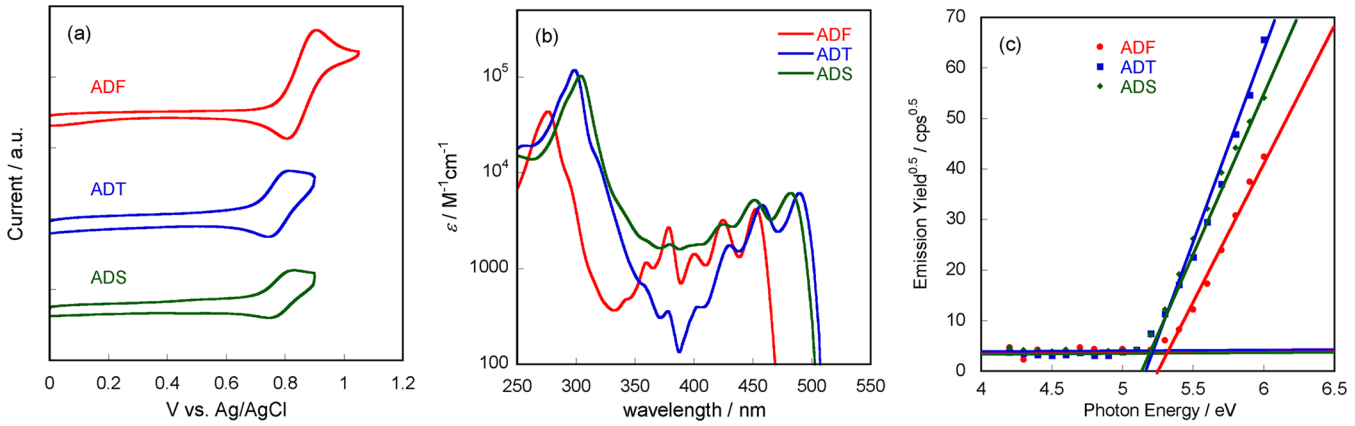


Figure 2. Cyclic voltammograms (a), absorption spectra in dichloromethane (b), and photoelectron yield spectroscopy in air (PESA) (c) of *anti*-ADF, ADT, and ADS.

Table 1. Electronic Properties of Benzo-, Naphtho-, and Anthra-dichalcogenophenes

compd	E_{ox}/V[a]	E_{HOMO}/eV[b]	IP/eV[c]	λ_{max} (λ_{edge})/nm	E_g/eV[d]	E_{LUMO}/eV[e]
ADF	+0.79 (0.86)	−5.1	5.2	453 (468)	2.6	−2.5
ADT[4a]	+0.71 (0.77)	−5.0	5.1	489 (506)	2.4	−2.6[f]
ADS	+0.71 (0.77)	−5.0	5.1	481 (501)	2.4	−2.6[f]
NDF[14]	+1.13	−5.5	5.5	364 (375)	3.3	−2.2
NDT[3b,15]	+0.95 (1.01)	−5.3	5.4	401 (412)	3.0	−2.3
NDS[15]	+0.95 (1.01)	−5.3	5.4	401 (415)	3.0	−2.3
BDF[17b,22]	+1.40	−5.7	5.8	277 (308)	4.0	−1.8
BDT[13c]	+1.31	−5.6	5.7	335 (342)	3.6	−2.0
BDS[13c]	+1.19	−5.5	5.6	350 (359)	3.5	−2.0

[a]V vs Ag/AgCl in benzonitrile containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt. Oxidation onsets (E_{ox}) are reported for all the compounds, whereas for compounds giving reversible oxidation waves, half-wave oxidation potentials ($E^{1/2}{}_{ox}$) are given in the parentheses. All the potentials were calibrated with the Fc/Fc^+ ($E^{1/2}$ = +0.46 V measured under identical conditions). [b]Determined by a photoelectron yield spectroscopy in air (PESA, a Riken AC-2 model) using the powder samples. [c]Estimated with a following equation: E_{HOMO} (eV) = −4.4 − E_{onset}. [d]Calculated from λ_{edge}. [e]Estimated with a following equation: E_{LUMO} (eV) = E_{HOMO} + E_g. [f]Electrochemical reduction potential was observed at E_{red} (onset)= −1.65 V for ADT and E_{red} (onset) = −1.70 V for ADS, both of which correspond to E_{LUMO} = −2.7 eV.

The synthesis of *anti*-ADS was similarly done as in the case of *anti*-ADT with several modifications (Scheme 4). The first introduction of methylseleno groups with elemental selenium and methyl iodide proceeded smoothly, but was slightly less effective than the synthesis of the sulfur counterpart with dimethyl disulfide. On the other hand, the Sonogashira coupling of **16** with trimethylsilylacetylene did not take place, owing to steric or electronic effect of the adjacent bulky methylseleno group. Alternatively the Stille coupling with 1-tributylstannyl-2-trimethylsilylacetylene did work quite well to afford **17**, the precursor for the *anti*-ADS framework. The subsequent Larock selenophene annulation reaction gave **18** in an excellent yield, and the final reductive desilylation/deiodination effected by lithium aluminum hydride gave *anti*-ADS (Scheme 4).[18b]

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Molecular Electronic Properties. The molecular electronic properties of *anti* -ADF, -ADT, and -ADS were investigated by cyclic voltammetry (CV, Figure 2a), absorption spectra in solution (Figure 2b), and photoelectron yield spectroscopy in air (PESA, Figure 2c) using their powder samples. Summarized in Table 1 are the oxidation potentials (E_{ox}), estimated HOMO energy levels (E_{HOMO}), ionization potentials (IP), absorption peaks and edges (λ_{max}, λ_{edge}), HOMO−LUMO energy gaps (E_g) estimated from the absorption edges, and estimated LUMO energy levels, together with their benzo- and naphtho- counterparts (For CV, PESA, and absorption spectra, see Figure S1, Supporting Information).

In general, for all the chalcogenophene series, extension of the acene core gave higher-lying E_{HOMO} and smaller E_g as in the case for oligoacene series (e.g., anthracene, tetracene, and pentacene),[20] which can be well represented by the schematic energy diagram (Figure 3). On the other hand, the furan

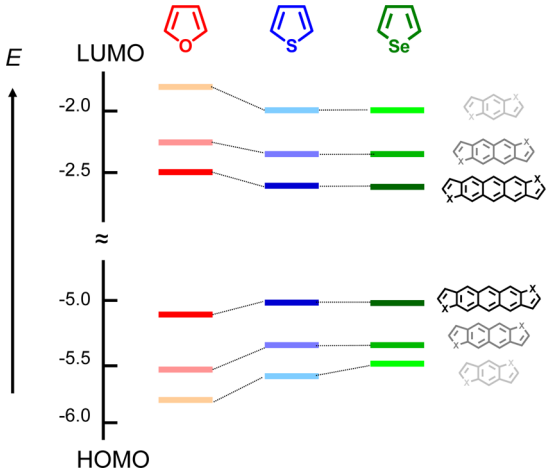

Figure 3. Schematic energy diagram of the linear-shaped acenedichalcogenophenes.

homologues in all the benzo-, naphtho-, and anthradichalcogenophene series tend to have lower-lying E_{HOMO} and larger E_g than those of the thiophene and selenophene counterparts. This can be explained by lower aromaticity of furan than those of thiophene/selenophene, limiting, as a result, the effective π-delocalization over the whole π-framework.[16,21]

It is interesting to note that all anthradichalcogenophenes (ADXs) show reversible oxidation peaks (Figure 2a). This is in sharp contrast to benzodichalcogenophenes (BDXs) and naphthodichalcogenophenes (NDXs), the former of which shows irreversible oxidation waves regardless of the chalcogenophene rings whereas the latter shows clear dependence on the chalcogenophene rings; only NDF shows irreversible oxidation wave (Figure S1, Supporting Information). The irreversibility of BDF and NDF was due to instability of the oxidized species, not polymerization on the working electrode,[16] and we thus concluded that the low aromaticity of the furan ring can not stabilize the cationic state of these lower homologues. On the other hand, the reversible oxidation wave of ADF indicates that the oxidized species (radical cation) can be stabilized by delocalization over the anthracene core, which is quite characteristic for ADF.

E_{HOMO}s estimated from the oxidation onsets are −5.1 eV for ADF and −5.0 eV for ADT/ADS. Although lower lying E_{HOMO}s of the furan compounds than the thiophene or selenophene counterparts and quite similar E_{HOMO}s for the thiophene or selenophene compounds are generally seen in BDX and NDX series (Table 1, Figure 3), the difference of E_{HOMO} (ΔE_{HOMO} = 0.1 eV) in the ADX series is rather smaller than those in the BDX and NDX series (ΔE_{HOMO} = 0.2 eV), indicating that the perturbation from the outermost chalcogenophene rings to the whole electronic structure is attenuated with the extension of the central acene system. Similar π-extension effects are also observed in E_gs estimated from the absorption edges; in the ADX series, the difference between ADF and ADT/ADS (ΔE_g) is 0.2 eV, whereas ΔE_gs for the BDX and NDX series are >0.4 and 0.3 eV, respectively. This can be also understood by considering the "dilution" effect of the perturbation from the outermost chalcogenophene rings by extending the central acene core. As a result, the ADF core turned out to be an interesting π-extended core that has the suitable HOMO energy level (−5.1 eV) as p-channel organic semiconductor both for good stability in ambient conditions and facile hole injection from metal electrode often used in OFETs such as gold.

FET Characteristics of *anti*-ADT and ADS. One of the primary objectives for the synthesis of isomerically pure *anti*-ADT is to elucidate the isomer effects on the device characteristics, especially field-effect mobility. In the Katz's pioneering works on ADTs, OFETs with the vapor deposited thin film of isomerically mixed ADT as the active channel showed the mobility of up to 0.09 $cm^2\ V^{-1}\ s^{-1}$ at the substrate temperature (T_{sub}) of 85 °C during vapor deposition.[4a] We fabricated *anti*-ADT-based vapor-processed OFETs at T_{sub} = 85 °C together with slightly lower T_{sub} (60 °C). As depicted in Figure 4a, the devices show typical FET responses, and the extracted mobility from the saturation regime are 0.3 $cm^2\ V^{-1}\ s^{-1}$ for both T_{sub} = 60 and 85 °C.

The mobility we obtained using the vapor deposited thin films, 0.3 $cm^2\ V^{-1}\ s^{-1}$, is in fact ca. three times higher than the value reported for the isomerically mixed ADT. In general, the device characteristics and extracted mobility largely depend on many factors, such as device structure, surface treatment, deposition rate, etc., it is hard to conclude with just the present experimental results that the devices based on isomerically pure *anti*-ADT is far superior than those with the isomerically mixed ADT. In the case of diphenyl derivatives of linear-shaped BDSs[2b,22] and NDTs,[3c] the device characteristics based on isomerically pure *syn* and *anti* compounds were compared under identical experimental conditions and device configurations, and the differences between the isomers were much pronounced; in both cases, *anti* derivatives gave higher mobility in the devices by ca. 1 order of magnitude. With these previous and present experimental results, we can say that isomerically pure *anti*-ADT tends to afford better mobility in OFETs than the isomerically mixed ADT does, but the difference is not very large. The smaller difference than those in the NDT and BDS cases could be interpreted by the π-extension effect in the ADT case; largely π-extended ADT tends to have small electrical and structural perturbation from the outermost thiophene rings than those in the case of the BDS and NDT derivatives. These speculations are also supported by recent results on isomerically pure *syn*- and *anti*- dimethyl-ADT derivatives.[12]

We also fabricated ADF- and ADS-based OFETs. The vapor deposited thin films of ADF, however, readily resublimed during the deposition of gold source and drain electrode, and thus evaluation of ADF thin film as an active layer in OFETs were failed in our device configuration with the bottom-gate

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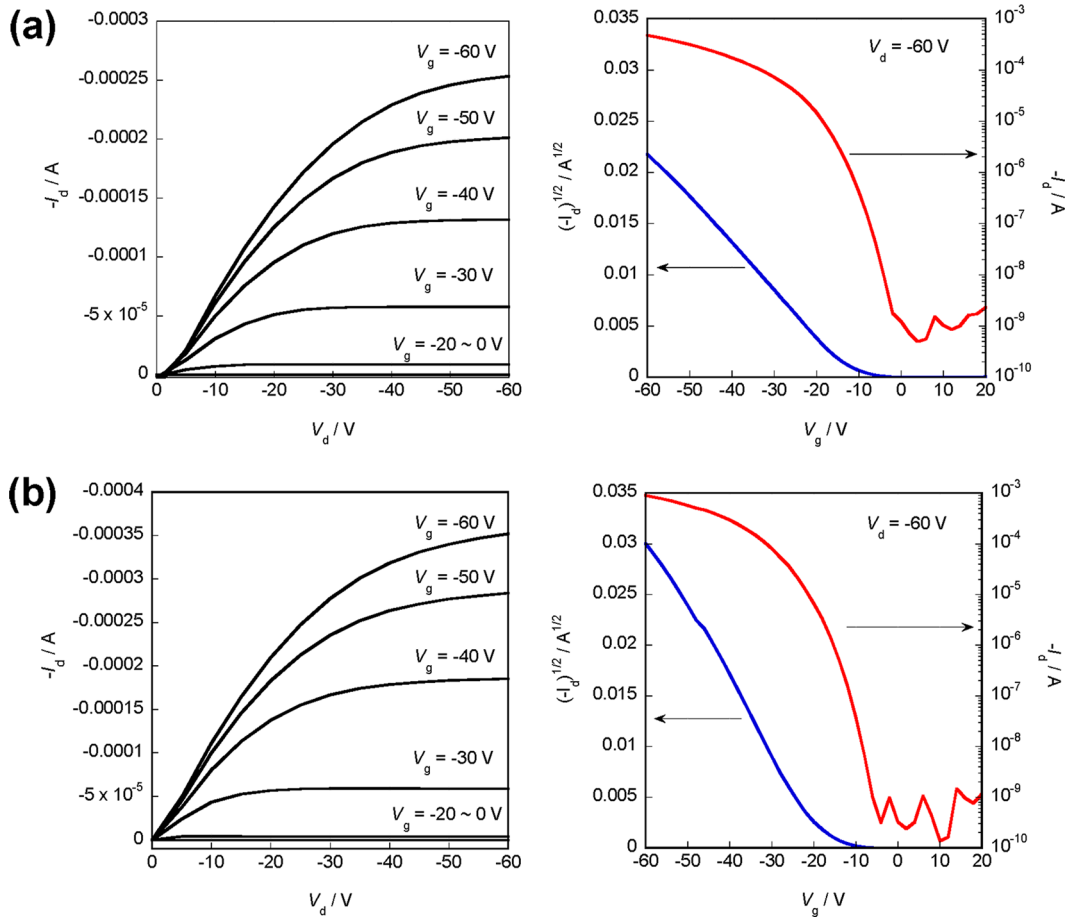

Figure 4. Output and transfer characteristics of (a) *anti*-ADT-based and (b) *anti*-ADS-based OFETs fabricated on octadecyltrichlorosilane (ODTS)-SAM modified Si/SiO_2 substrates at T_{sub} = 85 °C.

and top contact source and drain electrodes. This is attributed to a lower sublimation point of ADF than that of ADT, which means that the packing energy of the ADXs is affected by the chalcogen atoms, suggesting that the packing effectiveness and intermolecular interactions in the solid state are also affected by the chalcogen atoms. On the other hand, *anti*-ADS behaved as a good organic semiconductor similar to its sulfur counterpart: typical FET responses were observed for *anti*-ADS-based OFETs with extracted mobility of up to 0.7 cm^2 V^{-1} s^{-1} at T_{sub} = 85 °C (Figure 4b). These FET results indicate that the present *anti*-anthradichalcogenophenes are quite promising π-extended core for organic semiconductors, though the high volatility of parent ADF unfortunately prevent its evaluation as an organic semiconductor. Several furan-based π-extended materials have recently been investigated as promising organic semiconductors,[23,24] and in this regard, *anti*-ADF framework should also be interesting, provided that appropriate molecular modification is done. For this reason, we then synthesized and evaluated diphenyl derivative of ADF together with the counterparts of ADT and ADS.

Diphenyl Anthradichalcogenophenes (DPh-ADXs) for OFETs. The synthesis of DPh-ADXs are shown in Scheme 5, which is basically the same as for the synthesis of the parent systems: introduction of the phenyl substituents at the ADX precursor stage readily afford corresponding DPh-ADXs in acceptable yields, which means that the present synthetic routes to ADX derivatives are versatile for further development of ADX-based organic semiconductors.

All *anti*-DPh-ADXs are poorly soluble compounds and were purified by repeated vacuum sublimation. Their vapor-processed OFET devices including DPh-ADF-based ones showed typical OFET characteristics under ambient conditions (Figure 5). The best mobilities obtained were 0.6 cm^2 V^{-1} s^{-1} for DPh-ADF, 1.3 cm^2 V^{-1} s^{-1} for DPh-ADT, and 0.5 cm^2 V^{-1} s^{-1} for DPh-ADS. Compared to the mobility of the parent ones, DPh-ADT gave better mobility than the parent by several times, whereas the DPh-ADS-based device showed slightly lower mobility.

It is also interesting to note that these mobility values are similar to those of DPh-NDX series, but fairly higher than those of DPh-BDX series, implying that saturation of mobility with extension of acenedichalcogenophene cores is observed in the thin film transistor setting (Figure 6).[2b,16,25]

■ CONCLUSION

We have successfully established selective synthetic routes to anthra[2,3-*b*:6,7-*b*′] -difuran (*anti*-ADF), -dithiophene (*anti*-ADT), and -diselenophene (*anti*-ADS) from readily available 2,6-dimethoxyanthracene via selective functionalization at 3- and 7-positions as a key step. Although the synthesis of ADFs went straightforward as its lower analogue, NDFs, the syntheses of ADT and ADS via heteroannulation reactions using sodium chalcogenide reagents did not work, and thus alternative approach consisting of the Larock's thiophene or selenophene formation followed by reductive deiodination and desilylation was developed for the reproducible syntheses of *anti*-ADT and

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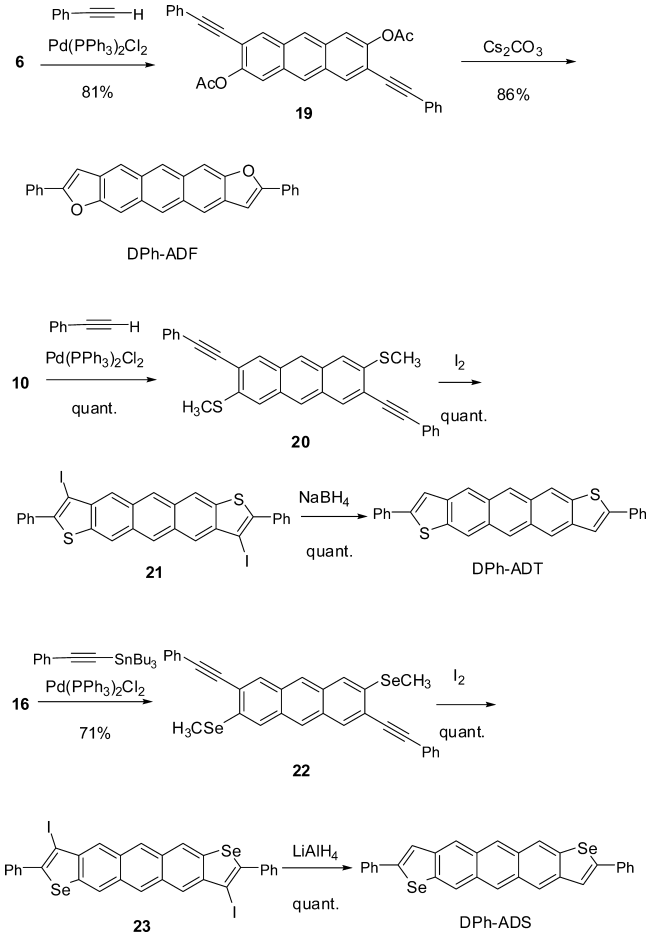
Scheme 5. Synthesis of *anti*-DPh-ADXs



ADS. The selective formation of the *anti*-isomer by the routes was confirmed by ^{13}C NMR spectra as well as single crystal X-ray analysis. The physicochemical properties of parent *anti*-ADXs investigated by cyclic voltammograms, UV−vis absorption spectra, and PESA, clearly indicated that *anti*-ADXs have relatively high-lying HOMO energy levels (∼−5.0 eV) and small HOMO−LUMO energy gap (∼2.4 eV). Comparison of these electronic properties with those of the lower analogues, BDXs and NDXs, can give insight into the electronic structure trend of acenedichalocogenophenes as the balance between the central acene core and the outermost chalcogenophene rings. Among isomerically pure parent *anti*-anthradichalcogenophenes, *anti*-ADT and *anti*-ADS can afford crystalline thin films by vapor deposition, which acted as active layer in organic field-effect transistors with mobility as high as 0.3 $cm^2\ V^{-1}\ s^{-1}$ for ADT and 0.7 $cm^2\ V^{-1}\ s^{-1}$ for ADS, respectively. The mobility of isomerically pure *anti*-ADT is higher by several times than those reported for isomercally mixed ADT, implying that there could exist an isomer effect on the field-effect mobility, but not significant. Considering the large *syn/anti* isomer effects on FET characteristics previously reported for DPh-BDS and DPh-NDT, the present small influence can be understood by the dilution effect of the central acene part; largely π-extended ADT tends to have small electrical and structural perturbation from the outermost thiophene rings than those in the case of the BDS and NDT derivatives. We then tested the diphenyl derivatives of *anti*-ADF, -ADT, and -ADS as the active material for OFET devices, which showed high mobilities of up to 1.3 $cm^2\ V^{-1}\ s^{-1}$. These mobilities observed for DPh-ADX-based OFETs were almost similar to those for DPh-NDX-based OFETs, implying that there could be a certain upper limit of the mobility with extension of the acenedichalcogenophene cores. With all these studies on *anti*-anthradichalcogenophene from their synthetic chemistry to OFET applications, we would like to place an emphasis on the potential of isomerically pure *anti*-anthradichalcogenophenes as a key component of organic electronics in future.

EXPERIMENTAL SECTION

Synthesis General. All chemicals and solvents are of reagent grade unless otherwise indicated. Triethylamine, ethanol, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA) were purified with standard distillation procedures prior to use. 2,6-Dimethoxyanthracene[14] was prepared according to the reported procedure. All reactions were carried out under nitrogen atmosphere. Melting points were uncorrected. Nuclear magnetic resonance spectra were obtained in deuterated chloroform ($CDCl_3$) or deuterated dimethylsulfoxide (DMSO-d_6) with teteramethylsilane (TMS) as internal reference; chemical shifts (δ) are reported in parts per million. EI-MS spectra were obtained using an electron impact ionization procedure (70 eV). The molecular ion peaks of the bromine, sulfur, or selenium containing compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{79}Br, ^{32}S, or ^{80}Se, respectively. All reported HRMS were obtained using an atmospheric pressure chemical ionization (APCI, vaporizer temperature: 400 °C) with a linear quadrupole ion trap (LTQ) or orbitrap method, except for **6**, where an electrospray ionization (ESI) with was used.

2,6-Dibromo-3,7-dimethoxyanthracene (2). To a suspension of 2,6-dimethoxyanthracene **1** (12 g, 50 mmol) in THF (2.0 L) was added 1.67 M hexane solution of *n*-BuLi (140 mL, 234 mmol) at 0 °C. After the mixture was stirred for 1 h at room temperature, 1,2-dibromo-1,1,2,2,-trichloroethane (100 g, 307 mmol) was added to the solution at 0 °C, and the resulting mixture was stirred for 12 h at room temperature. The mixture was poured into a saturated aqueous ammonium chloride solution (200 mL), and the organic solvent was removed by evaporation. The resulting precipitate was collected by filtration, washed with water, methanol and a small amount of chloroform, then dried in vacuo to give 2,6-dibromo-3,7-dimethoxyanthracene **2** (20.0 g, quantitative yield) as a pale-green solid. Mp 282−283 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 8.12 (s, 2H), 7.21 (s, 2H), 4.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 132.7, 124.0, 120.9, 115.0, 105.8, 90.1, 56.9; EI-MS (70 eV) m/z = 394 (M^+); HRMS (APCI): Calcd for $C_{16}H_{12}Br_2O_2$ 394.92768 [MH^+], found 394.92789.

3,7-Dibromoanthracene-2,6-diol (3). To a solution of 2,6-dibromo-3,7-dimethoxyanthracene **2** (25 g, 63 mmol) in dichloromethane (700 mL) was added dropwise a dichloromethane solution of BBr_3 (ca. 4 M, 50 mL, 100 mmol) at 0 °C. After refluxing for 12 h, crashed ice (ca. 100 g) was added to the mixture at 0 °C. The organic solvent was removed by evaporation, and the resulting precipitate was collected by filtration, washed with water and methanol, dried in vacuo to give 3,7-dibromoanthracene-2,6-diol **3** (23.2 g, quantitative yield) as a pale-green solid. Mp >300 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 10.61 (s, 2H), 8.27 (s, 2H), 8.20 (s, 2H), 7.31 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.2, 131.4, 129.9, 128.2, 122.3, 114.8, 107.8; IR (KBr) ν = 3359 cm^{-1} (OH); EI-MS (70 eV) m/z = 366 (M^+); HRMS (APCI): Calcd for $C_{14}H_9Br_2O_2$ 366.89638 [MH^+], found 366.89654.

2,6-Dibromo-3,7-bis(trifluoromethanesulfonyloxy)-anthracene (4). To a solution of 3,7-dibromoanthracene-2,6-diol **3** (5.0 g, 14 mmol) and triethylamine (10.0 mL, 71.4 mmol) in dichloromethane (400 mL) was added trifluoromethanesulfonic anhydride (7.0 mL, 42 mmol) at 0 °C. After stirring for 19 h at room temperature, the mixture was diluted with water (50 mL) and hydrochloric acid (4 M, 100 mL). The resulting mixture was extracted with dichloromethane (150 mL × 3). The combined organic layer was washed with brine (100 mL × 3), dried ($MgSO_4$), and purified by flash

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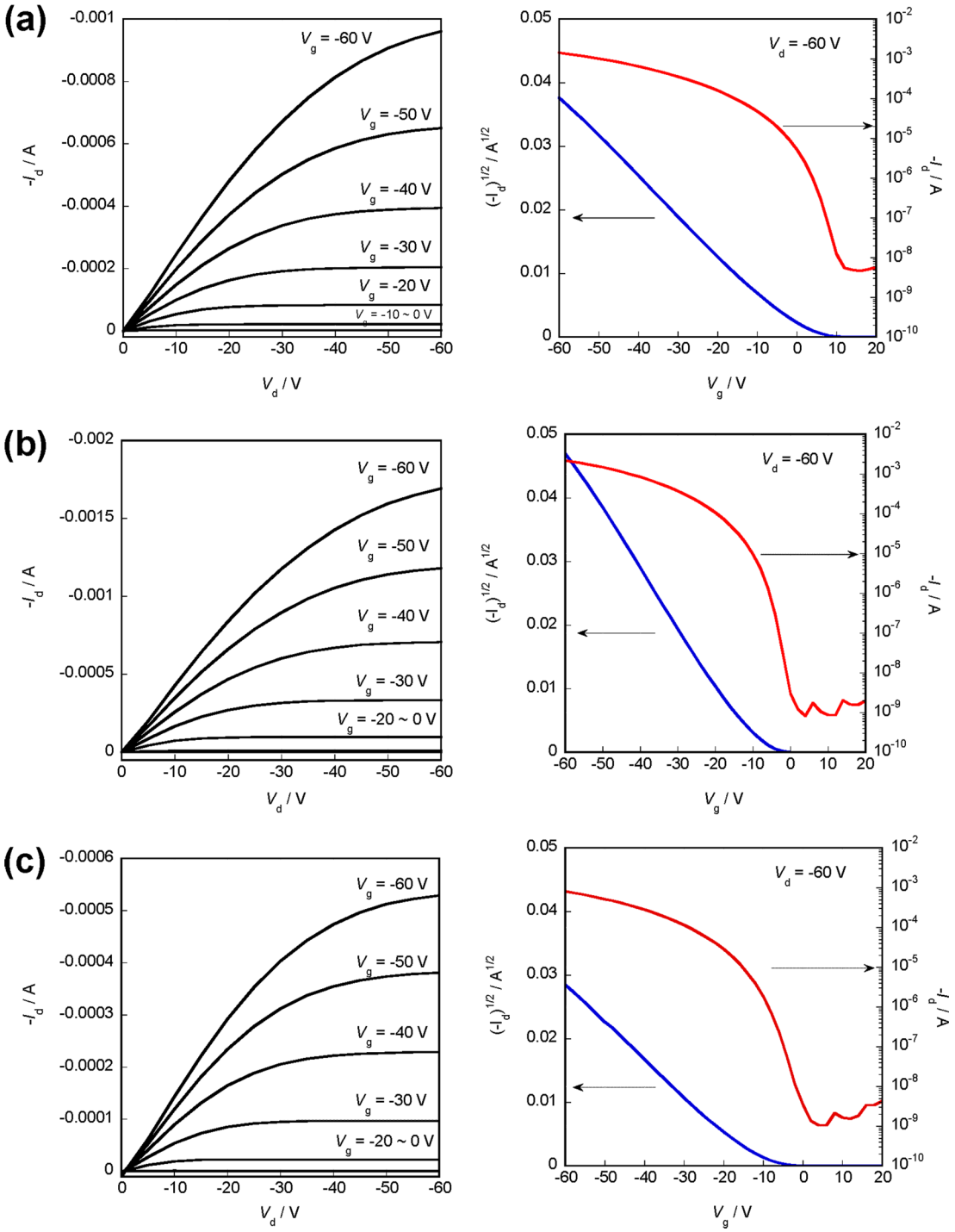

Figure 5. Output and transfer characteristics of (a) DPh-ADF-based, (b) DPh-ADT-based OFETs, (c) DPh-ADS-based OFETs fabricated on octadecyltrichlorosilane (ODTS)-SAM modified Si/SiO_2 substrates at T_{sub} = 150 °C.

column chromatography on silica gel (R_f = 0.5, dichloromethane/hexane, 1:1 v/v) to give 2,6-dibromo-3,7-bis(trifluoromethanesulfonyloxy)anthracene **4** (8.6 g, quantitative yield) as a yellow solid. Mp 232−233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.37 (s, 2H), 8.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.5, 131.8, 131.8, 131.2, 121.4, 117.8, 115.5; IR (KBr) ν = 1417, 1212 cm^{-1} (-O−SO_2-); EI-MS (70 eV) m/z = 630 (M^+); HRMS (APCI): Calcd for $C_{16}H_6F_6O_6S_2Br_2$ 629.78713 [M^+], found 629.78632.

2,6-Dibromo-3,7-bis(trimethylsilylethynyl)anthracene (5). To a deaerated solution of 2,6-dibromo-3,7-bis(trifluoromethanesulfonyloxy)anthracene **4** (1.0 g, 1.6 mmol) in triethylamine (10 mL) and DMF (10 mL) was added trimethylsilylacetylene (0.32 mL, 3.2 mmol), $Pd(PPh_3)_2Cl_2$ (56.2 mg, 0.080 mmol, 5 mol %) and CuI (30.5 mg, 0.16 mmol, 10 mol %). After stirring for 12 h at room temperature, the mixture was diluted with water (50 mL) and hydrochloric acid (4 M, 10 mL). The resulting precipitate was collected by filtration and washed with water. The solid was purified by flash column chromatography on silica-gel (R_f = 0.6, dichloromethane/hexane, 1:1 v/v) to gave 2,6-dibromo-3,7-bis(trimethylsilylethynyl)-anthracene **5** (437 mg, 56%) as a pale-yellow solid. Mp 281−282 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 8.19 (s, 2H), 8.17 (s, 2H), 0.32 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 134.0, 131.8, 131.2, 125.6, 123.2, 122.0, 103.3, 100.8, 0.14; EI-MS (70 eV)

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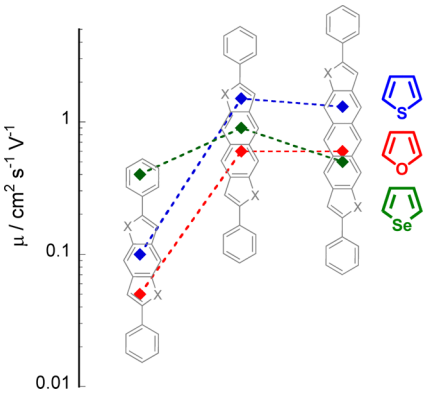

Figure 6. Mobility dependence on the chalcogenophene rings and central acene cores in diphenyl-acenedichalcogenophene series.

m/z = 526 (M^+). HRMS (APCI): Calcd for $C_{24}H_{24}Br_2Si_2$ 525.97778 [M^+], found 525.97723.

2,6-Diacetoxy-3,7-dibromoanthracene (6). To a suspension of 3,7-dibromoanthracene-2,6-diol **3** (5.0 g, 14 mmol) and triethylamine (15 mL, 107 mmol) in dichloromethane (400 mL) was added acetic anhydride (3.4 mL, 36 mmol) at 0 °C. After the mixture was stirred for 7 h at room temperature, the mixture was diluted with water (100 mL) and hydrochloric acid (4 M, 100 mL). The organic solvent was removed by evaporation, and the resulting precipitate was collected by filtration, washed with water and small amount of chloroform, and then dried in vacuo to give 2,6-diacetoxy-3,7-dibromoanthracene **6** as a white solid (2.7 g, 43%). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 2H), 8.25 (s, 2H), 7.75 (s, 2H), 2.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 145.6, 132.6, 131.0, 130.9, 125.5, 120.6, 116.7, 20.8; IR (KBr) ν = 1763 cm^{-1} (C═O); EI-MS (70 eV) m/z = 450 (M^+). HRMS (ESI): Calcd for $C_{18}H_{12}Br_2O_4$ 472.89946 [MNa^+], found 472.89948.

2,6-Diacetoxy-3,7-bis(trimethylsilylethynyl)anthracene (7). To a deaerated solution of 2,6-deacetoxy-3,7-dibromoanthracene **6** (1.8 g, 4.0 mmol) in triethylamine (20 mL) and DMF (20 mL) was added trimethylsilylacetylene (1.2 mL, 9.6 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol, 5.0 mol %) and CuI (76.2 mg, 0.4 mmol, 10 mol %). After stirring for 12 h at 60 °C, the mixture was diluted with water (10 mL) and hydrochloric acid (4 M, 20 mL). The resulting precipitate was collected by filtration and washed with water, which was further purified by flash column chromatography on silica-gel (R_f = 0.3, dichloromethane/hexane, 1:1 v/v) to give 2,6-diacetoxy-3,7-bis-(trimethylsilylethynyl)anthracene **7** (1.6 g, 84%) as a yellow solid. Mp 232−233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 2H), 8.18 (s, 2H), 7.65 (s, 2H), 2.40 (s, 6H), 0.30 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 147.9, 134.6, 131.4, 130.4, 126.5, 119.4, 117.8, 100.8, 100.4, 21.2, 0.24; IR (KBr) ν = 1774 cm^{-1} (C═O); EI-MS (70 eV) m/z = 486 (M^+). HRMS (APCI): Calcd for $C_{28}H_{30}O_4Si_2$ 487.17554 [MH^+], found 487.17480.

Anthra[2,3-*b*:6,7-*b*′]difuran (*anti*-ADF). To a suspension of cesium carbonate (6.0 g, 18 mmol) in DMA (50 mL) and water (6 mL) was added 2,6-diacetoxy-3,7-bis(trimethylsilylethynyl)anthracene **7** (1.0 g, 2.1 mmol), and the resulting mixture was then stirred at 80 °C for 4 h. The mixture was poured into 200 mL of saturated aqueous ammonium chloride solution, and the resulting precipitate was collected by filtration and washed with water to give anthra[2,3-*b*:6,7-*b*′]difuran (0.33 g, 63%) as a yellow solid. Analytical sample was obtained by repetitive gradient sublimation in vacuo (ca. 240 °C at <10^{-2} Pa under nitrogen atmosphere) and solvent washing (chloroform). Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 2H), 8.35 (s, 2H), 8.17 (s, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.07(d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.5, 149.1, 129.7, 129.1, 129.0, 125.5, 118.2, 106.3, 105.0; EI-MS (70 eV) m/z = 258 (M^+). Anal. Calcd for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90%. Found C, 83.77; H, 4.11%; HRMS (APCI): Calcd for $C_{18}H_{10}O_2$ 259.07536 [MH^+], found 259.07547.

2,6-Dimethoxy-3,7-bis(methylthio)anthracene (8). To a suspension of 2,6-dimethoxyanthracene **1** (16.5 g, 69 mmol) in THF (2.0 L) was added 1.62 M hexane solution of *n*-BuLi (175 mL, 276 mmol) at 0 °C. After the mixture was stirred for 1 h at room temperature, dimethyldisulfide (31 mL, 345 mmol) was added to the mixture at 0 °C, and the resulting mixture was stirred for 9 h at room temperature. The mixture was poured into a saturated aqueous ammonium chloride solution (500 mL), and the organic solvent was removed by evaporation. The resulting precipitate was collected by filtration, washed with water, and then dissolved in chloroform. The solution was dried ($MgSO_4$), and concentrated in vacuo. The residue was then purified by flash column chromatography on silica gel (R_f = 0.7, dichloromethane/hexane, 1:1 v/v) to give analytically pure 2,6-dimethoxy-3,7-bis(methylthio)anthracene **8** (22.7 g, quantitative yield) as a pale-yellow solid. Mp 253−255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.50 (s, 2H), 7.12 (s, 2H), 4.03 (s, 6H), 2.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 130.7, 129.5, 128.3, 122.4, 122.0, 103.3, 55.9, 14.5; EI-MS (70 eV) m/z = 330 (M^+). Anal. Calcd for $C_{18}H_{18}O_2S_2$: C, 65.42; H, 5.49%. Found: C, 65.47; H, 5.34%.

3,7-Bis(methylthio)anthracene-2,6-diol (9). To a solution of 2,6-dimethoxy-3,7-bis(methylthio)anthracene **8** (14 g, 42 mmol) in dichloromethane (2 L) was added dropwise a dichloromethane solution of BBr_3 (ca. 4 M, 40 mL, 160 mmol) at 0 °C. After the mixture was stirred for 18 h at room temperature, crashed ice (ca. 100 g) was added to the mixture at 0 °C. The organic solvent was removed by evaporation and the resulting precipitate was collected by filtration, washed with water, and dried in vacuo to give practically pure 3,7-bis(methylthio)anthracene-2,6-diol **9** (12.7 g, quantitative yield) as a pale-green solid. Mp 252−255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 8.05 (s, 2H), 7.36 (s, 2H), 6.37 (s, 2H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 132.9, 131.6, 129.2, 127.3, 123.7, 107.8, 19.4; IR (KBr) ν = 3396 cm^{-1} (OH); EI-MS (70 eV) m/z = 302 (M^+). Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.55; H, 4.67%. Found: C, 63.32; H, 4.42%.

2,6-Bis(methylthio)-3,7-bis(trifluoromethanesulfonyloxy)-anthracene (10). To a suspension of 3,7-bis(methylthio)anthracene-2,6-diol **9** (10 g, 33 mmol) and triethylamine (30 mL, 214 mmol) in dichloromethane (500 mL) was added trifluoromethanesulfonic anhydride (15 mL, 89 mmol) at 0 °C. After stirring for 20 h at room temperature, the mixture was diluted with water (100 mL) and hydrochloric acid (4 M, 100 mL). Evaporation of the organic solvent in vacuo gave a precipitate, which was collected by filtration, washed with water and small amount of chloroform, them dried in vacuo to give 2,6-bis(trifluoromethanesulfonyloxy)-3,7-bis(methylthio)-anthracene **10** (10.5 g, 56%) as a yellow solid. Mp 212−213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 2H), 7.86 (s, 2H), 7.73 (s, 2H), 2.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 132.2, 130.6, 130.0, 125.9, 125.6, 120.5, 119.1, 117.3, 15.6; IR (KBr) ν = 1429, 1222 cm^{-1} (-O−SO_2-); EI-MS (70 eV) m/z = 566 (M^+). Anal. Calcd for $C_{18}H_{12}F_6O_6S_4$: C, 38.16; H, 2.13%. Found C, 38.37; H, 1.83%.

2,6-Bis(methylthio)-3,7-bis(trimethylsilylethynyl)anthracene (11). To a deaerated solution of 2,6-bis(trifluoromethanesulfonyloxy)-3,7-bis(methylthio)anthracene **10** (283 mg, 0.5 mmol) in triethylamine (5.0 mL) and DMF (5.0 mL) was added trimethylsilylacetylene (0.17 mL, 1.2 mmol), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 0.025 mmol, 5 mol %) and CuI (9.5 mg, 0.05 mmol, 10 mol %). After stirring for 12 h at 60 °C, the mixture was diluted with water (10 mL) and hydrochloric acid (4 M, 2.0 mL). The resulting precipitate was collected by filtration and washed with water. The solid was purified by flash column chromatography on silica-gel (R_f = 0.5, dichloromethane/hexane, 1:1 v/v) to give 2,6-bis(methylthio)-3,7-bis(trimethylsilylethynyl)-anthracene **11** (230 mg, quantitative yield) as a pale yellow solid Mp 210−213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 8.05 (s, 2H), 7.47 (s, 2H), 2.60 (s, 6H), 0.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 133.5, 131.5, 130.4, 124.9, 121.4, 120.7, 102.7, 102.1, 15.8, 0.51; EI-MS (70 eV) m/z = 462 (M^+). Anal. Calcd for $C_{26}H_{30}S_2Si_2$: C, 67.47; H, 6.53%. Found: C, 67.32; H, 6.40%.

3,9-Diiodo-2,8-bis(trimethylsilyl)anthra[2,3-*b*:6,7-*b*′]-dithiophene (12). To a solution of 2,6-bis(methylthio)-3,7-bis-(trimethylsilylethynyl)anthracene **11** (2.9 g, 6.3 mmol) in dichloro-

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methane (200 mL) was added iodine (8.0 g, 31 mmol) at 0 °C. After stirring for 3 h at room temperature, the mixture was poured into a vigorously stirred aqueous solution of sodium hydrogen sulfite (50 mL). The resulting precipitate was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give crude 3,9-diiodo-2,8-bis(trimethylsilylethynyl)anthra[2,3-*b*:6,7-*b*′]dithiophene **12** (4.1 g, 88%) as a dark reddish solid. Mp 250 °C (Decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 2H), 8.52 (s, 2H), 8.51 (s, 2H), 0.56 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.4, 137.6, 129.8, 129.6, 126.1, 124.1, 119.9, 86.9, 0.8; EI-MS (70 eV) m/z = 686 (M^+). Anal. Calcd for $C_{24}H_{24}I_2S_2Si_2$: C, 41.99; H, 3.52%. Found: C, 42.00; H, 3.22%.

Anthra[2,3-*b*:6,7-*b*′]dithiophene (*anti*-ADT). To a suspension of 3,9-diiodo-2,8-bis(trimethylsilyl)anthra[2,3-*b*:6,7-*b*′]dithiophene **12** (2.0 g, 2.9 mmol) in ethanol (200 mL) was added sodium borohydride (8.0 g, 31 mmol). The mixture was then reflux for 24 h. After cooling to 0 °C, hydrochloric acid (4M, 50 mL) was added to the mixture with stirring (ca. 10 min) to precipitate a dark-red solid. The solid was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give crude anthra[2,3-*b*:6,7-*b*′]dithiophene (4.1 g, 88%) as an orange solid. Analytical sample was obtained by repetitive gradient sublimation in vacuo (ca. 290 °C at $<10^{-2}$ Pa under nitrogen atmosphere) and solvent washing (chloroform). Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 2H), 8.69 (s, 2H), 8.63 (s, 2H), 7.75 (d, J = 5.2 Hz, 2H), 7.51 (d, J = 5.2 Hz, 2H); EI-MS (70 eV) m/z = 290 (M^+). Anal. Calcd for $C_{18}H_{10}S_2$: C, 74.45; H, 3.47%. Found: C, 74.18; H, 3.22%; HRMS (APCI): Calcd for $C_{18}H_{10}S_2$ 291.02967 [MH^+], found 291.02991. The solubility of *anti*-ADT was not sufficient for measuring ^{13}C NMR spectra.

3,9-Diphenylanthra[2,3-*b*:6,7-*b*′]dithiophene (13). To a degassed suspension of 3,9-diiodo-2,8-bis(trimethylsilyl)anthra[2,3-*b*:6,7-*b*′]dithiophene **12** (69 mg, 0.1 mmol), phenylboronic acid (36.6 mg, 0.3 mmol) and $K_3PO_4{\cdot}nH_2O$ (200 mg) in DMF (3.0 mL) was added $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 10 mol %) at 90 °C. After stirring for 15 h, the resulting mixture was poured into a saturated aqueous sodium hydrogen sulfite solution (50 mL) with stirring (ca. 10 min). The resulting precipitate was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and recrystallization from $CHCl_3$ to give 3,9-dipheynyl-anthra[2,3-*b*:6,7-*b*′]dithiophene **13** (30 mg, 68%) as a dark-red solid. Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 2H), 8.60 (s, 2H), 8.56 (s, 2H), 7.72 (d, J = 8.0 Hz, 4H), 7.59 − 7.49 (m, 6H), 7.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ138.5, 137.8, 137.2, 135.9, 129.4, 129.1, 128.9, 128.8, 127.9, 125.9, 125.7, 121.3, 120.8; EI-MS (70 eV) m/z = 442 (M^+); HRMS (APCI): Calcd for $C_{30}H_{18}S_2$ 442.08444 [M^+], found 442.08450.

2,6-Dimethoxy-3,7-bis(methylseleno)anthracene (14). To a suspension of 2,6-dimethoxyanthracene **1** (12 g, 50 mmol) in THF (2.0 L) was added 1.67 M hexane solution of *n*-BuLi (140 mL, 234 mmol) at 0 °C. After the mixture was stirred for 1 h at room temperature, selenium powder (16.6 g, 210 mmol) was added to the solution at 0 °C, and the resulting mixture was stirred for 30 min at room temperature to give a clear solution of corresponding selenoate. Iodomethane (15 mL, 243 mmol) was then added to the solution at 0 °C and the mixture was stirred for 12 h. The mixture was poured into a saturated aqueous ammonium chloride solution (500 mL), and evaporation of the organic solvent in vacuo gave a precipitate, which was collected by filtration, washed with water and methanol, then dried in vacuo to give 2,6-dimethoxy-3,7-bis(methylseleno)anthracene **14** (16.0 g, 76%) as a white solid. Mp 267−268 °C (Decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.62 (s, 2H), 7.11 (s, 2H), 4.02 (s, 6H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 130.1, 128.8, 125.9, 125.4, 122.5, 103.1, 55.9, 5.0; EI-MS (70 eV) m/z = 426 (M^+). HRMS (APCI): Calcd for $C_{18}H_{18}O_2Se_2$ 426.97100 [MH^+], found 426.97018.

3,7-Bis(methylseleno)anthracene-2,6-diol (15). To a solution of 2,6-dimethoxy-3,7-bis(methylseleno)anthracene **14** (14 g, 33 mmol) in dichloromethane (2 L) was added dropwise a dichloromethane solution of BBr_3 (ca. 4 M, 50 mL, 200 mmol) at 0 °C. After the mixture was stirred for 12 h at room temperature, crashed ice (ca. 100 g) was added to the mixture at 0 °C. The organic solvent was removed by evaporation and the resulting precipitate was collected by filtration. The crude product was washed successively with water and small amount of ethanol and chloroform, and dried in vacuo to give sufficiently pure 3,7-bis(methylseleno)anthracene-2,6-diol **15** (13.0 g, quantitative yield) as a pale-green solid. Mp 272−273 °C (Decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 8.13 (s, 2H), 7.36 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 135.5, 131.8, 129.1, 123.6, 122.9, 107.1, 9.7; IR (KBr) ν = 3404 cm^{-1} (OH); EI-MS (70 eV) m/z = 398 (M^+); HRMS (APCI): Calcd for $C_{16}H_{14}O_2Se_2$ 398.93970 [MH^+], found 398.93930.

2,6-Bis(methylseleno)-3,7-bis(trifluoromethanesulfonyloxy)anthracene (16). To a suspension of 3,7-bis(methylseleno)-anthracene-2,6-diol **15** (12 g, 30 mmol) and triethylamine (40.0 mL, 285 mmol) in dichloromethane (700 mL) was added trifluoromethanesulfonic anhydride (15 mL, 89 mmol) at 0 °C. After the mixture was stirred for 3 h at room temperature, the mixture was diluted with water (100 mL) and hydrochloric acid (4 M, 100 mL). The resulting mixture was extracted with dichloromethane (400 mL × 3). The combined organic layers were washed with brine (400 mL × 3), dried ($MgSO_4$) and purified by flash column chromatography on silica-gel (R_f = 0.3, dichloromethane/hexane, 1:1 v/v) to give 2,6-bis(methylseleno)-3,7-bis(trifluoromethanesulfonyloxy)anthracene **16** (7.5 g, 38%) as a yellow solid. Mp 223−224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.90 (s, 2H), 7.88 (s, 2H), 2.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9 130.8, 130.4, 129.8, 126.1, 125,7, 118.7, 7.2; IR (KBr) ν = 1425, 1222 cm^{-1} (-O−SO_2-); EI-MS (70 eV) m/z = 662 (M^+); HRMS (APCI): Calcd for $C_{18}H_{12}O_6F_6S_2Se_2$ 661.83044 [M^+], found 661.82971.

2,6-Bis(methylseleno)-3,7-bis[(trimethylsilyl)ethynyl]anthracene (17). To a deaerated solution of 2,6-bis(methylseleno)-3,7-bis(trifluoromethanesulfonyloxy)anthracene **16** (1.50 g, 2.27 mmol) in DMF (40 mL) were added trimethyl[(tributylstannyl)-ethynyl]silane (2.2 g, 5.68 mmol) and $Pd(PPh_3)_2Cl_2$ (79.7 mg, 0.114 mmol, 5 mol %). After stirring for 2 h at 60 °C, the mixture was diluted with water (10 mL) and hydrochloric acid (4 M, 2.0 mL). The resulting precipitate was collected by filtration and washed with water. The solid was purified by flash column chromatography on silica-gel (R_f = 0.3, dichloromethane/hexane, 1:1 v/v) to give 2,6-bis-(methylthio)-3,7-bis[(trimethylsilyl)ethynyl]anthracene **17** (1.02 g, 81%) as a pale-yellow solid. Mp 227−228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 8.05 (s, 2H), 7.67 (s, 2H), 2.46 (s, 6H), 0.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 132.7, 131.6, 130.6, 125.3, 124.9, 122.2, 103.4, 101.3, 6.84, 0.25; EI-MS (70 eV) m/z = 558 (M^+); HRMS (APCI): Calcd for $C_{26}H_{30}Se_2Si_2$ 558.02110 [M^+], found 558.02063.

3,9-Diiodo-2,8-bis(trimethylsilyl)anthra[2,3-*b*:6,7-*b*′]-diselenophene (18). To a solution of 2,6-bis(methylseleno)-3,7-bis[(trimethylsilyl)ethynyl]anthracene **17** (0.557 g, 1.0 mmol) in dichloromethane (60 mL) was added iodine (1.01 g, 4 mmol) at 0 °C. After stirring for 3 h at room temperature, the mixture was poured into a saturated aqueous sodium hydrogen sulfite solution (5 mL) with stirring (ca. 10 min). The resulting precipitate was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give 3,9-diiodo-2,8-bis(trimethylsilyl)-anthra[2,3-*b*:7,8-*b*′] diselenophene **18** (0.694 g, 89%) as a dark-reddish solid. Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 2H), 8.59 (s, 2H), 8.54 (s, 2H), 0.55 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 137.7, 130.7, 127.9, 126.7, 124.0, 114.4, 99.8, 98.6, 0.28; EI-MS (70 eV) m/z = 782 (M^+). HRMS (APCI): Calcd for $C_{24}H_{24}I_2Se_2Si_2$ 781.78302 [M^+], found 781.78308.

Anthra[2,3-*b*:6,7-*b*′]diselenophene (*anti*-ADS). To a suspension of 3,9-diiodo-2,8-bis(trimethylsilyl)anthra[2,3-*b*:6,7-*b*′]-diselenophene **18** (0.50 g, 0.64 mmol) in 1,4-dioxane (100 mL) was added $LiAlH_4$ (0.5 g, 13.2 mmol), and the mixture was refluxed for 24 h; ethyl acetate (50 mL) was then added to the mixture at 0 °C with stirring (ca. 10 min). The resulting precipitate was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give anthra[2,3-*b*:6,7-*b*′]diselenophene

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(0.21 g, 86%) as an orange solid. The solid was purified by repetitive gradient sublimation in vacuo (ca. 310 °C at $<10^{-2}$ Pa under nitrogen atmosphere) and solvent washing (chloroform). Mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.76 (s, 2H), 8.74 (s, 2H), 8.61 (s, 2H), 8.17 (d, J = 5.2 Hz, 2H), 7.71 (d, J = 5.2 Hz, 2H); EI-MS (70 eV) m/z = 386 (M^+); HRMS (APCI): Calcd for $C_{18}H_{10}Se_2$ 385.91075 [M^+], found 385.91040. The solubility of *anti*-ADS was not sufficient for measuring ^{13}C NMR spectra.

2,6-Diacetoxy-3,7-bis(phenylethynyl)anthracene (19). To a deaerated solution of 2,6-diacetoxy-3,7-dibromoanthracene **6** (1.8 g, 4.0 mmol) in triethylamine (20 mL) and DMF (20 mL) were added phenylacetylene (0.98 g, 9.6 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol, 5 mo l%), and CuI (76.2 mg, 0.4 mmol, 10 mol %). After stirring for 12 h at 60 °C, the mixture was diluted with water (10 mL) and hydrochloric acid (4 M, 20 mL). The resulting precipitate was collected by filtration and washed with water, methanol, and dichloromethane to give 2,6-diacetoxy-3,7-bis(phenylethynyl)-anthracene **19** (1.6 g, 81%) as a yellow solid. Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 2H), 8.26 (s, 2H), 7.73 (s, 2H), 7.56−7.55 (m, 4H), 7.40−7.39 (m, 6H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7,146.3,140.4, 139.1, 133.7, 133.3, 130.3, 129.9, 12.7, 122.5, 118.8, 144.0,93.9, 23.3; IR (KBr) ν = 1752.36 cm^{-1} (C═O); EI-MS (70 eV) m/z = 494 (M^+). HRMS (APCI): Calcd for $C_{34}H_{22}O_4$ 494.15126 [M^+], found 494.15195.

2,8-Diphenylanthra[2,3-*b*:6,7-*b*′]difuran (DPh-ADF). To a suspension of cesium carbonate (6.0 g, 18 mmol) in DMA (200 mL) and water (24 mL) were added 2,6-diacetoxy-3,7-bis-(phenylethynyl)anthracene **19** (1.04 g, 2.1 mmol), and the resulting mixture was then stirred at 100 °C for 24 h. After poured into 200 mL of saturated aqueous ammonium chloride solution, the precipitate was collected by filtration and washed with water to give 2,8-diphenylanthra[2,3-*b*:6,7-*b*′]difuran (0.740 g, 86%) as an orange solid. The solid was purified by repetitive gradient sublimation in vacuo (ca. 280 °C at $<10^{-2}$ Pa under nitrogen atmosphere) and solvent washing (chloroform). Mp >300 °C; EI-MS (70 eV) m/z = 410 (M^+). HRMS (APCI): Calcd for $C_{30}H_{18}O_2$ 410.13013 [M^+], found 410.13120. The solubility of DPh-ADF was not sufficient to obtain ^{1}H and ^{13}C NMR spectra useful for structural characterization.

2,6-Bis(methylthio)-3,7-bis(phenylethynyl)anthracene (20). To a deaerated solution of 2,6-bis(methylthio)-3,7-bis-(trifluoromethanesulfonyloxy)anthracene **10** (283 mg, 0.5 mmol) in triethylamine (5.0 mL) and DMF (5.0 mL) were added phenylacetylene (1.23 g, 1.2 mmol), $Pd(PPh_3)_2Cl_2$ (17.6 mg, 0.025 mmol, 5 mol %), and CuI (9.5 mg, 0.05 mmol, 10 mol %). After stirring for 12 h at 60 °C, the mixture was diluted with water (10 mL) and hydrochloric acid (4 M, 2.0 mL). The resulting precipitate was collected by filtration and washed with water. The solid was purified by flash column chromatography on silica-gel (R_f = 0.6, dichloromethane/hexane, 1:1 v/v) to give 2,6-bis(methylthio)-3,7-bis(phenylethynyl)-anthracene **20** (234 mg, quantitative yield) as a pale-yellow solid. Mp 222−223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 2H), 8.10 (s, 2H), 7.66−7.64 (m, 4H), 7.52 (s, 2H), 7.40−7.38 (m, 6H), 2.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ138.1, 132.8, 132.3, 131.6, 130.5, 129.2, 129.0, 124.9, 123.6, 121.6, 120.9, 96.4, 87.8, 15.9; EI-MS (70 eV) m/z = 470 (M^+). Anal. Calcd for $C_{32}H_{22}S_2$: C, 81.66; H, 4.71%. Found C, 81.56; H, 4.69%.

3,9-Diiodo-2,8-diphenylanthra[2,3-*b*:6,7-*b*′]dithiophene (21). To a solution of 2,6-bis(methylthio)-3,7-bis(phenylethynyl)-anthracene **20** (2.96 g, 6.3 mmol) in dichloromethane (200 mL) was added iodine (8.0 g, 31 mmol) at 0 °C. After stirring for 3 h at room temperature, the mixture was poured into a vigorously stirred aqueous solution of sodium hydrogen sulfite (50 mL). The resulting precipitate was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give crude 3,9-diiodo-2,8-diphenylanthra[2,3-*b*:6,7-*b*′]dithiophene **21** (4.71 g, quantitative yield) as a dark-reddish solid. Analytical sample was obtained by recrystallization from chlorobenzene. Mp >300 °C; EI-MS (70 eV) m/z = 694 (M^+). Anal. Calcd for $C_{30}H_{16}I_2S_2$: C, 51.89; H, 2.32%. Found: C, 52.11; H, 2.42%. Poor solubility of **21** did not allow its characterization by means of ^{1}H and ^{13}C NMR spectra.

2,8-Diphenylanthra[2,3-*b*:6,7-*b*′]dithiophene (DPh-ADT). To a suspension of 3,9-diiodo-2,8-diphenylanthra[2,3-*b*:6,7-*b*′]-dithiophene **21** (2.17 g, 2.9 mmol) in ethanol (200 mL) was added sodium borohydride (8.0 g, 31 mmol). The mixture was then reflux for 24 h. After cooling to 0 °C, hydrochloric acid (4M, 50 mL) was added to the mixture with stirring (ca. 10 min) to precipitate a dark red solid. The solid was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give crude 2,8-diphenylanthra[2,3-*b*:6,7-*b*′]dithiophene (DPh-ADT, 1.28 g, quantitative yield) as a dark-reddish solid. The solid was purified by repetitive gradient sublimation in vacuo (ca. 320 °C at $<10^{-2}$ Pa under nitrogen atmosphere) and solvent washing (chloroform) for device fabrication. Mp > 300 °C; EI-MS (70 eV) m/z = 442 (M^+). Anal. Calcd for $C_{30}H_{18}S_2$: C, 81.41; H, 4.10%. Found: C, 81.49; H, 4.11%. The solubility of DPh-ADT was too low to obtain ^{1}H and ^{13}C NMR spectra for structural characterization.

2,6-Bis(methylseleno)-3,7-bis(phenylethynyl)anthracene (22). To a deaerated solution of 2,6-bis(trifluoromethanesulfonyloxy)-3,7-bis(methylseleno)anthracene **16** (1.50 g, 2.27 mmol) in DMF (40 mL) was added tributyl(phenylethynyl)tin (2.22 g, 5.68 mmol), $Pd(PPh_3)_2Cl_2$ (79.7 mg, 0.11 mmol, 5 mol %). After stirring for 2 h at 60 °C, the mixture was diluted with water (10 mL) and hydrochloric acid (4 M, 2.0 mL). The resulting precipitate was collected by filtration and washed with water. The solid was purified by flash column chromatography on silica-gel (R_f = 0.6, dichloromethane/hexane, 1:1 v/v) to give 2,6-bis(methylseleno)-3,7-bis(phenylethynyl)anthracene **22** (0.91 g, 71%) as a pale-yellow solid. Mp 227−228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 8.13 (s, 2H), 7.74 (s, 2H), 7.66−7.64 (m, 4H), 7.40−7.38 (m, 6H), 2.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.2, 132.5, 132.3, 131.9, 130.9, 129.2, 129.0, 125.6, 125.2, 123.5, 122.6, 95.6, 88.6, 7.06; EI-MS (70 eV) m/z = 564 (M^+); HRMS (APCI): Calcd for $C_{32}H_{22}Se_2$ 566.00465 [M^+], found 566.00598.

3,9-Diiodo-2,8-diphenylanthra[2,3-*b*:6,7-*b*′]diselenophene (23). To a solution of 2,6-bis(methylseleno)-3,7-bis(phenylethynyl)-anthracene **22** (0.566 g, 1.0 mmol) in dichloromethane (60 mL) was added iodine (1.01 g, 4 mmol) at 0 °C. After stirring for 3 h at room temperature, the mixture was poured into a saturated aqueous sodium hydrogen sulfite solution (5 mL) with stirring (ca. 10 min). The resulting precipitate was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give 3,9-diiodo-2,8-bis(trimethylsilylethynyl)anthra[2,3-*b*:6,7-*b*′]-diselenophene **23** (0.788 g, quant) as a dark-reddish solid, which was sufficiently pure for the characterization and next reaction. Mp >300 °C; EI-MS (70 eV) m/z = 788 (M^+). HRMS (APCI): Calcd for $C_{30}H_{16}I_2Se_2$ 789.76663 [M^+], found 789.76819. The solubility of compound **23** was not sufficient for measuring ^{1}H and ^{13}C NMR spectra.

2,8-Diphenylanthra[2,3-*b*:6,7-*b*′]diselenophene (DPh-ADS). To a suspension of 3,9-diiodo-2,8-diphenylanthra[2,3-*b*:6,7-*b*′]-diselenophene **23** (0.504 g, 0.64 mmol) in THF (100 mL) was added $LiAlH_4$ (0.5 g, 13.2 mmol), and the mixture was refluxed for 24 h. After cooling, ethyl acetate (50 mL) was added to the mixture at 0 °C with stirring (ca. 10 min). The resulting precipitate was collected by filtration, washed successively with water (100 mL) and ethanol (100 mL), and dried in vacuo to give 2,8-diphenylanthra[2,3-*b*:6,7-*b*′]diselenophene (0.343 g, quantitative yield) as a dark-reddish solid. The solid was purified by repetitive gradient sublimation in vacuo (ca. 360 °C at $<10^{-2}$ Pa under nitrogen atmosphere) and solvent washing (chloroform) for device fabrication. Mp >300 °C; EI-MS (70 eV) m/z = 536 (M^+); HRMS (APCI): Calcd for $C_{30}H_{19}Se_2$ 538.98117 [MH^+], found 538.98096. The solubility of DPh-ADS was not sufficient for measuring ^{1}H and ^{13}C NMR spectra.

Device Fabrication. Si/SiO_2 substrates were exposed to ODTS (octadecyltrichlorosilane) vapor at room temperature in a closed desiccator under nitrogen overnight. OFETs were fabricated in a "top-contact" configuration on a heavily doped n^+-Si (100) wafer with a 200 nm thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}). Thin film (50 nm thick) of ADX derivatives as an active layer was vacuum-deposited on the Si/SiO_2 substrate maintained at various temperatures (T_{sub}) at a deposition rate of ca. 1 Å s^{-1} under a pressure of ~10^{-3} Pa. On top of

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the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (L) and width (W) are 40 μm and 3.0 mm, respectively. Characteristics of the OFET devices were measured at room temperature in the air with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility (μ_{FET}) was calculated in the saturation regime (V_d = −60 V) of the I_d using the following equation,

$$I_d = (WC_i/2L)m_{FET}(V_g - V_{th})^2$$

where C_i is the capacitance of the SiO_2 insulator, and V_g and V_{th} are the gate and threshold voltages, respectively. Current on/off ratio (I_{on}/I_{off}) was determined from the I_d at V_g = 0 V (I_{off}) and V_g = −60 V (I_{on}). The μ_{FET} data reported in Table S1 (Supporting Information) are typical values from more than five different devices.

Physicochemical Studies. UV−vis spectra were measured in dichloromethane or chloroform solution (concentration: 10^{-5}∼10^{-6} M). Cyclic voltammograms (CVs) were recorded in benzonitrile containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc^+: $E^{1/2}$ = +0.46 V measured under identical conditions). X-Ray diffractions of thin films deposited on the Si/SiO_2 substrate were obtained with a CuKα source (λ = 1.541 Å) in the air. Ionization potentials (IPs) were determined with photoemission yield spectroscopy in air. AFM images of thin films on Si/SiO_2 were obtained with a tapping mode in air.

■ ASSOCIATED CONTENT

Supporting Information

Instrumentation for the characterization of compounds, AFM images of vapor deposited thin films of *anti*-ADF, *anti*-ADT, *anti*-ADS, DPh-ADF, DPh-ADT, and DPh-ADS on Si/SiO_2 substrates, absorption spectra and cyclic voltammograms of *anti*-BDF/BDT/BDS and NDF/NDT/NDS, NMR spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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