Fluorine-containing Diethynyl Aryl Derivatives for n-Channel Organic Field-effect Transistors

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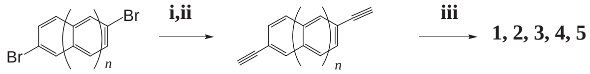
Fluorine-containing diethynyl aryl derivatives (**1**–**5**), in which three aromatic rings were connected together with rigid acetylenic linkages, were synthesized for n-channel organic field-effect transistors. The field-effect electron mobility of the thin film of **2** exhibited $3.4 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$.

Much attention has been paid on the development of organic semiconductors for applications to various low-cost, large-area, and flexible electronics, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells. Until now, various classes of organic semiconductors have been investigated for OFETs.[1] It is well known that acene derivatives or thiophene derivatives show a high field-effect mobility.

Many conventional organic semiconductors show p-channel conductions in OFETs, whereas some specific materials with much lower highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels show n-channel OFET characteristics. Because introducing fluorine atoms to molecules enhances electron affinity in π-conjugated systems, some fluorine-containing materials are known to show n-channnel conduction in OFETs.[2] The utilization of electron-withdrawing fluorine-containing aromatic rings connect with acetylenic linkage is promising for realizing the materials with high electron affinity suitable for n-channel OFETs.

In this work, we designed a series of linear molecules, in which three aromatic rings are connected together with rigid acetylenic linkages. Two end aromatic groups are pentafluorophenyl or heptafluoronaphthyl groups. We report herein the synthesis and characterization of five diethynyl aryl derivatives as shown in Figure 1, 2,6-bis[(pentafluorophenyl)ethynyl]naphthalene (**1**), 2,6-bis[(heptafluoronaphthalen-2-yl)ethynyl]naphthalene (**2**), 2,6-bis[(pentafluorophenyl)ethynyl]anthracene (**3**), 2,6-bis[(heptafluoronaphthalen-2-yl)ethynyl]anthracene (**4**), and 2,6-bis[(heptafluoronaphthalen-2-yl)ethynyl]benzene (**5**). Furthermore, these derivatives have been evaluated for OFETs and found that the three compounds having heptafluoronaphthyl group (**2**, **4**, and **5**) have exhibited n-channel OFET characteristics.

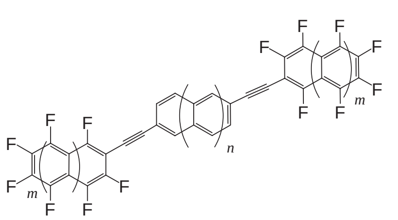


6 2,6-Diethynylnaphthalene ($n = 1$)
7 2,6-Diethynylanthracene ($n = 2$)
1,4-Diethynylbenzene ($n = 0$) is commercially available.

Scheme 1. Synthesis of compounds **1**–**5** (i) 2-methylbut-3-yn-2-ol, $Pd(PPh_3)_4$, CuBr, LiBr, in Et_3N, THF, 90–95 °C (ii) KOH in paraffin oil, 110–130 °C/30 mmHg (iii) bromopentafluorobenzene or 2-bromoheptafluoronaphthalene, $Pd(PPh_3)_4$, CuBr, in Et_3N, Toluene, 90–95 °C.

Scheme 1 shows the synthesis of **1**–**5**. 2,6-Diethynylnaphthalene and 2,6-diethynylanthracene were synthesized in two steps from 2,6-dibromonaphthalene and 2,6-dibromoanthracene by palladium-catalyzed coupling reaction with 2-methylbut-3-yn-2-ol and a subsequent base-induced retro-Favorsky reaction.[3] 2,6-Diethynylnaphthalene and 2,6-diethynylanthracene were converted to **1**, **2**, **3**, and **4**, respectively by using palladium-catalyzed coupling reaction with bromopentafluorobenzene[4] or 2-bromoheptafluoronaphthalene in moderate yield. Commercially available 1,4-diethynylbenzene was converted to **5** by using the same method. All compounds were purified by sublimation, and the structures were determined by ^{19}F and ^{1}H NMR, mass spectrometry, and IR spectrum.[5]

We fabricated OFETs having a top contact geometry shown in Figure 2.[6] The organic semiconductors were vacuum-evaporated at below 2×10^{-6} Torr onto the substrate at room temperature. Three derivatives having heptafluoro naphthyl group (**2**, **4**, and **5**) exhibited n-channel OFET behavior under positive gate bias conditions. On the other hand, two derivatives having pentafluorophenyl group (**1** and **3**) did not exhibited FET responses. Figure 3 shows the output and transfer characteristics for OFETs with **5** using Ca source–drain (S–D) electrodes. The OFET characteristics (field-effect mobilities (μ_{FET}), and threshold voltages (V_{T}) and on/off ratios) of **2**, **4**, and **5** are summarized in Table 1.



1 $m = 0, n = 1$
2 $m = 1, n = 1$
3 $m = 0, n = 2$
4 $m = 1, n = 2$
5 $m = 1, n = 0$

Figure 1. Structures of diethynyl benzene, naphthalene, and anthracene derivatives.

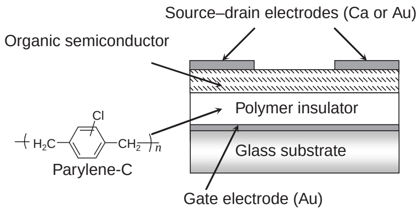


Figure 2. Schematic cross section of organic field-effect transistor in this study.

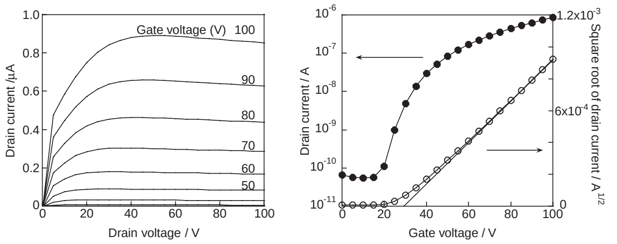


Figure 3. (a) Plots of drain current versus drain voltage at various gate voltage values for OFETs using **5** and Ca source–drain electrodes. (b) Plots of drain current (left) and square root of drain current (right) versus gate voltage at drain voltage of 100 V for the OFETs.

For the purpose of examining the effects of fluorine substitutions, we synthesized an all hydrocarbon type of **2**, 2,6-bis-[(naphthalen-2-yl)ethynyl]naphthalene (**8**) in two steps from 2,6-dibromonaphthalene with the same method of Scheme 1. The OFET with **8** was fabricated with the previously described method except for using Au as source–drain electrode. The OFET exhibited only p-channel behavior under negative gate bias conditions. As has been well known in several materials, such as pentacene, phthalocyanine, thiophene derivatives, and phenylenevinylene oligomers, the carrier conduction in OFETs can be converted from p-channel to n-channel by introducing fluoro substituents.[2] The field-effect hole mobility, on/off ratio and threshold gate voltage for **8** are included in Table 1.

The energy levels of HOMO of condensed matters were estimated by a photoelectron yield spectroscopic method with an AC-3 spectrometer.[7] HOMO–LUMO energy gaps (E_g) of these derivatives were estimated from absorption spectra edge measured with evaporated thin films, and the energy levels of the LUMO were calculated from the equation LUMO $=$ HOMO $- E_g$. The HOMO and LUMO levels for **1**–**5** and **8** are shown in Table 1. Fluorine-substituted compounds have lower HOMO and LUMO levels than their hydrocarbon analogues. The comparison between **2** and **8**, which have the same carbon skeletons, may elucidate the roles of fluorine substitution on end naphthyl groups. The fluorine substitution gives a HOMO level shift of 0.55 eV accompanied by a small increase of E_g of 0.05 eV. Thus, the contribution of lowering the LUMO level by the fluorine substitution is very large, as large as 0.5 eV. The LUMO shift of 0.5 eV is good enough for changing p-channel to n-channel OFET characteristics.

X-ray diffraction (XRD) patterns of the films were examined. The films of **2**, **5**, and **8**, gave strong diffraction intensities, with the primary diffraction peak appearing at 3.70° (spacing of 23.89 Å) for **2**, at 4.03° (spacing of 21.93 Å) for **5** and 3.55° (spacing of 24.90 Å) for **8**. Comparisons of the observed interlayer spacing with the molecular length of **2** (25.75 Å), for example, indicated that the long axis of **2** might be slightly inclined away from the direction normal to the substrate. This means that the π–π stacking direction is parallel to a substrate, favorable for in-plane charge transport. On the other hand, XRD patterns of the films of **1**, **3**, and **4** gave no peak corresponding to the interlayer spacing.[5] This observation suggested that the films were amorphous or that π–π stacking directions were not parallel to substrates. From the XRD data, the presence of the large central core of anthracene unit **4** or the smaller end perfulorophenyl ring **1** and **3** is suggested to prevent the growth of highly oriented crystalline textures, favorable for high FET mobilities.

Table 1. OFET characteristics and HOMO, LUMO energy levels of **1**–**5** and **8**

Compound	S–D electrodes	Channel	μ_{FET} /cm^2 V^{-1} s^{-1}	V_T /V	On/off ratio	HOMO /eV	LUMO /eV
1	Ca	—	no FET	—	—	6.39	3.60
2	Ca	n	3.4×10^{-3}	48	5.4×10^{3}	6.15	3.28
2	Au	n	6.8×10^{-4}	71	1.3×10^{2}	—	—
3	Ca	—	no FET	—	—	6.58	3.88
4	Ca	n	2.7×10^{-4}	20	7.9×10^{2}	5.95	3.36
5	Ca	n	1.3×10^{-3}	29	2.4×10^{4}	6.10	3.16
5	Au	n	1.9×10^{-4}	61	8.5×10^{2}	—	—
8	Au	p	6.4×10^{-3}	−64	2.1×10^{4}	5.60	2.68

Two derivatives **1** and **3**, that have not shown any n-channel characteristics, have lower LUMO levels than other fluorine-containing derivatives **2**, **4**, and **5**. That indicates organic semiconductors **1** and **3** have a smaller electron-injection barrier than other ones. So the reason why OFETs with **1** or **3** have not exhibited any n-channel behavior is obviously ascribed to the crystalline structure of the films.

In conclusions, we have developed and characterized new fluorine-containing diethynyl aryl derivatives for n-channel OFETs. The field-effect electron mobilities of the thin film of **2**, **4**, and **5** were 3.4×10^{-3}, 2.7×10^{-4}, and 1.2×10^{-3} cm^2 V^{-1} s^{-1}, and on/off ratios for **2**, **4**, and **5** were 5.4×10^{3}, 7.9×10^{2}, and 1.6×10^{4}, respectively. The substitution of hydrogen atoms on the end naphthalene rings in **8** to fluorine atoms brought about the 0.5 eV LUMO level shift, and this shift caused the change of carrier conduction from p-channel to n-channel.

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