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Fluoro-substituted Phenyleneethynylenes: Acetylenic n-Type Organic Semiconductors

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Fluoro-substituted phenyleneethynylenes are synthesized by Sonogashira coupling and acetylide-nucleophilic substitution of fluorobenzenes. Fluoro-substitution of benzenes enables deep LUMO potential, and CF_3-substitution provides high electron mobility in deposited film ($\mu = 5.5 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$).

A number of organic materials with highly expanded π systems have been developed for organic field-effect transistors[1] (OFET) and organic light-emitting diodes[2] (OLED). Fluoro- and fluoroalkyl-substituted arenes have attracted great attention, because they have low-energy LUMO and may serve as electron-transporting materials.[3] Although a number of n-type OFET devices have been fabricated by using electron-transporting materials,[4] carrier mobilities observed in the devices are insufficient for practical use, and further development of organic semiconducting material with high mobility is still necessary. We have been involved in synthesis of phenyleneethynylene derivatives[5] and succeeded in application of CF_3-substituted phenyleneethynylene **1** (Figure 1) to n-type organic semiconductor material by invoking the carrier-transporting properties of phenyleneethynylene array and electron-withdrawing effect of CF_3 groups.[6] We envisioned that fluoro-substituted phenyleneethynylenes could serve more efficiently as n-type semiconductors, because fluorines on benzenes would give rise to deep HOMO and LUMO levels. We present herein synthesis of **2**–**9**, their cyclic voltammograms and preliminary results of OFET properties using **9** as n-type semiconducting material.

In Scheme 1 are shown representative synthetic processes for **4**, **6**, and **9**.[7,8] Decafluorodiphenylethyne (**10**) was prepared in 55% yield by coupling between **11** and **12** in the presence of 5 mol % of palladium catalyst and a stoichiometric amount of copper(I) chloride. The target compound **4** was synthesized in 60% yield by substitution at 4- and 4′-positions of **10** with lithium phenylethynide. Similar substitution at the 4-position of **10** with lithium ethynide which was prepared by lithiation of **13** afforded nonafluoro-derivative **6** in 65% yield. In this substitution reaction, a large excess of **10** was required in order to suppress formation of bis-adduct, and when only two equivalents of **10** was used, the yield of **6** decreased to 18%. Terminal ethyne **13** was provided by Sonogashira coupling between trimethylsilylethyne and **14**, followed by removal of the TMS group, which had been obtained by one-shot double elimination between benzyl sulfone **15** and iodobenzaldehyde (**16**). Iodination of **17** with I_2/K_3PO_4 gave an iodide **18** in 55% yield, and Sonogashira coupling of **18** with trimethylsilylethyne provides an inseparable mixture of the desired product **19** and trimethylsilylethyne-homocoupling product **20** in 86% and 7% yield, respectively. Treatment of a THF solution of **19** (containing **20**)

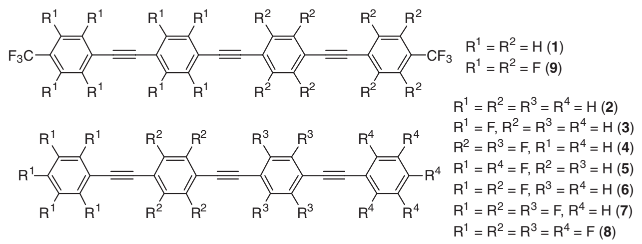
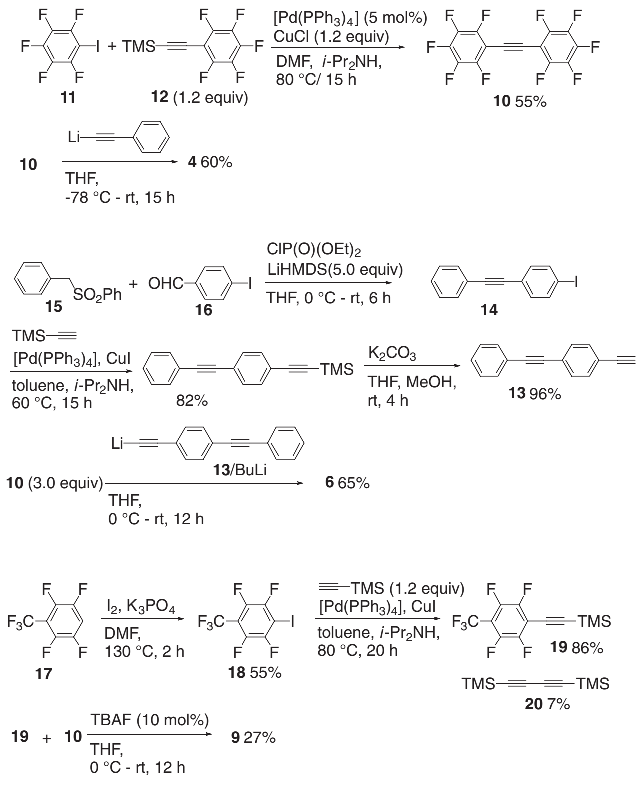


Figure 1. Structures of **1**–**9**.



Scheme 1. Synthetic processes for **4**, **6**, and **9**.

and **10** with tetrabutylammonium fluoride afforded **9** in 27% yield.

In order to assess the electronic effect of fluorine on HOMO and LUMO potentials, cyclic voltammograms of **2**–**9** were recorded in THF by using $Ag/AgNO_3$ as a reference electrode, and the half-wave reduction potentials E_{red} for **2**–**9** are summarized in Table 1.[8,9] Fluoro-substituted phenyleneethynylenes **3**–**9** undergo reversible electrochemical reduction at −1.20 to −2.02 V, while **2** does not. It is observed that reduction potential

Table 1. Electrochemical properties and HOMO and LUMO energy levels of **2**–**9**

Compound	E_{red}[a,b]	E_{LUMO}[a,d]	E_{HOMO}[a,d]	ΔE[a,d,e]
2	—	—	—	3.31
		(−2.10)	(−5.47)	(3.37)
3	−2.02	−2.36	−5.62	3.26
		(−2.26)	(−5.58)	(3.32)
4	−1.57	−2.81	−5.99	3.18
		(−2.64)	(−5.90)	(3.26)
5	−1.97	−2.41	−5.72	3.31
		(−2.37)	(−5.72)	(3.35)
6	−1.66	−2.72	−5.86	3.14
		(−2.56)	(−5.75)	(3.19)
7	−1.40	−2.98	−6.16	3.18
		(−2.77)	(−6.01)	(3.24)
8	−1.33[c]	−3.05	−6.27	3.22
		(−2.88)	(−6.18)	(3.30)
9	−1.20[c]	−3.18	−6.40	3.22
		(−3.05)	(−6.34)	(3.29)

[a]V. [b]Half-wave reduction potential ($Ag/AgNO_3$, in THF (1.0×10^{-3} M for **3**–**7**)). [c]Concentration is unknown because of poor solubility of **8** and **9**. [d]Calculated results on B3LYP/6-31G(d) in parentheses. [e]HOMO–LUMO energy gap.

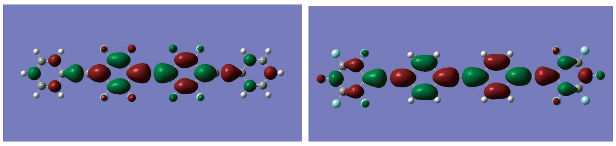


Figure 2. (a) LUMO of **4**. (b) LUMO of **5**.

E_{red} gradually shifted to higher potential in accordance with the number of fluorines on benzene rings: $E_{red} = -2.02$ V for **3**, −1.97–−1.57 V for **4**–**6**, −1.40 V for **7**, −1.33 V for **8**, and −1.20 V for **9**. This shows that fluorine on benzene rings serves as an electron-withdrawing group resulting in deep LUMO potentials as we expected.

The ionization potentials (E_{HOMO}) and electron affinities (E_{LUMO}) of **2**–**9** were estimated by their reduction potential E_{red} and HOMO–LUMO energy gap which were calculated from the corresponding wavenumber of UV–vis absorption edge (Table 1).[9,10]

DFT calculations (B3LYP/6-31G(d)) were carried out for planar conformers of **2**–**9** by taking solvent effect ($\varepsilon_{THF} = 7.43$) into consideration,[11] and the calculated HOMO and LUMO level potentials are shown in Table 1 as well. It is found that both E_{LUMO} and E_{HOMO} potentials experimentally obtained are consistent with those obtained from DFT calculation. Notably, fluoro-substitution on internal benzene enables deeper E_{LUMO} potential than substitution on terminal benzene: $E_{red} = -1.57$ V for **4** vs. −1.97 V for **5**. The deeper E_{LUMO} potential in **4** can be explained by participation of whole fluorines on internal benzenes in the LUMO. As shown in Figure 2, coefficients of the LUMO are located on all fluorines in **4**, and *eight* fluorine atoms serve as electron-withdrawing group resulting in the deep LUMO potential, while in **5**, fluorines at 3- and 5-positions of terminal benzenes are located on nodes of the LUMO giving rise to participation of only *four* fluorine atoms in the LUMO.

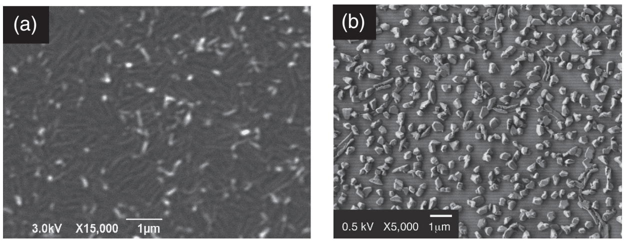


Figure 3. (a) SEM of **9**. (b) SEM micrograph of **4**.

Table 2. Field-effect transistor characteristics of **9**-deposited devices

Entry	Surface[a]	T /°C[b]	Mobility μ /$cm^2 V^{-1} s^{-1}$	On/off ratio	Threshold /V
1	Si	25	5.5×10^{-2}	10^5	45
2	H	25	5.2×10^{-2}	10^6	30
3	H	60	5.2×10^{-2}	10^6	40

[a]Si: SiO_2, H: HMDS-treated SiO_2. [b]Temperature of SiO_2 substrate on vacuum deposition.

Terminal CF_3 groups serve more efficiently as electron-withdrawing groups than fluorine, and CF_3-substituted derivative **9** exhibited by 0.13 V deeper E_{LUMO} and E_{HOMO} potentials in comparison to those of F-substituted derivative **8**.

Finally, we prepared vacuum-deposition films of **2**–**9** on SiO_2 at 25 °C and investigated their microstructures by using scanning electron microscopy (SEM). As shown in Figure 3a, the SEM micrograph of film of **9** demonstrates highly packed polycrystalline texture with a number of protrusions, while investigation of other fluoro derivatives **3**–**8** displays isolated circular features or porous morphologies (micrograph of **4** is shown in Figure 3b, representatively). Because substitution of benzenes with CF_3 groups enables highly ordered structure of **9** as well as deeper reduction potential, high electron transport could be expected for OFET devices fabricated from **9**. A field-effect transistor device was fabricated from **9** using a top-contact configuration: a 50-nm-thick fluorophenyleneethynylene **9** layer was deposited on Si/SiO_2 or hexamethyldisilazane (HMDS)-treated Si/SiO_2 substrate at 25 or 60 °C under vacuum (ca. 10^{-5} Torr). The electrical measurements were performed in a cryostat under vacuum at 25 °C because the device exhibited unstable FET operation in air. Table 2 shows FET properties such as mobility, on/off ratio, and threshold voltage, and Figure 4 displays drain current (I_d)–drain voltage (V_d) plots operating at different gate voltages (V_g) and I_d– and $I_d^{1/2}$–V_g plots (representative, for Entry 2 in Table 2). The fluoro derivative **9** exhibited n-type characteristics as expected, and FET response was observed at high gate voltage (>30 V). Equation 1 demonstrates rather high field-effect electron mobility of **9** ($\mu = 5.2$–$5.5 \times 10^{-2}\,cm^2 V^{-1} s^{-1}$), and this reveals that fabrication conditions such as treatment of Si/SiO_2 substrate and temperature provide no influence on the mobility of **9**.

$$I_d = W\mu C(V_g - V_{th})^2/2L \quad (1)$$

I_d: drain current (μA), W: channel width (mm), μ: mobility ($cm^2 V^{-1} s^{-1}$), C: capacitance of SiO_2 insulator (1.18×10^{-8} $F cm^{-2}$), V_g: gate voltage (V), V_{th}: threshold voltage (V), and L: channel length (μm).

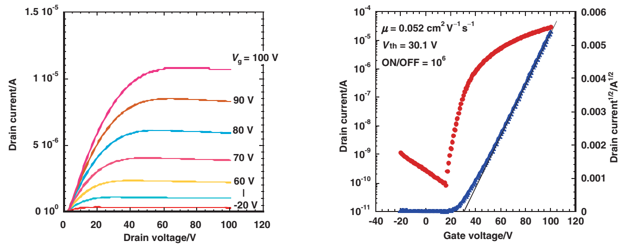


Figure 4. FET properties of **9** film deposited on HMDS-treated SiO_2 (Entry 2 in Table 2). (a) Drain current (I_d) versus drain voltage (V_d) characteristics as a function of gate voltage (V_g). (b) I_d and $I_d^{1/2}$ versus V_g plots.

In summary, we established synthetic processes for a series of fluoro-substituted phenyleneethynylenes and revealed that substitution of benzenes with fluorine enabled low LUMO potential both in terms of electrochemistry and ab initio calculation. CF_3-Substituted fluorophenyleneethynylene **9** exhibited rather deep reduction potential in cyclic voltammetry and provided a finely π-stacked structure in vacuum-deposited film. An FET device fabricated by use of **9** showed n-type properties ($\mu = 5.5 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$) as expected from its deep reduction potential. Further research in application of a series of fluoro-substituted phenyleneethynylenes to n-type semiconductors is underway.

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7 Representative synthetic procedure for **9** was shown in Supporting Information, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

8 Syntheses, characterization, and spectral data of **2**–**9** and procedure of preparation of FET devices and their properties will be described fully in the following full paper.

9 CV profile of **9** was representative shown in Figure S1.[7]

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11 The theoretical calculations of **2**–**9** were performed with the Gaussian 09 software package.

