# High Performance n- and p-Type Field-Effect Transistors Based on Tetrathiafulvalene Derivatives

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In the research field of organic field-effect transistors (OFETs),[1] thiophene oligomers[2] and acene molecules[3] have been extensively studied for over 20 years. The development of new materials is particularly important for the progress of this field. Tetrathiafulvalene (TTF) derivatives are promising candidates for semiconductors giving high performance FETs because of their self-assembling properties leading to strong intermolecular interactions.[4] However, because of the strong electron-donating properties, the thin films are generally labile to oxygen, resulting in poor FET performance.[5] In our previous work, we introduced fused aromatic rings or electron-deficient nitrogen heterocycles to the TTF skeleton to enhance the stability and obtained high hole mobilities in the thin films.[6] Compared to p-type semiconductors, the number of n-type semiconductors is still limited, and their FET performances are not satisfactory.[7] The development of good n-type materials is crucial for the fabrication of p−n junctions, bipolar transistors, and integrated circuits.[8] To obtain high electron mobility, organic semiconductors should have proper LUMO energy levels near the work function of electrodes.[9] High performance n-type organic semiconductors have recently been obtained by introducing electron-accepting substituents into electron-donating π-conjugated systems.[8a,10] Therefore, we have now introduced electron-withdrawing halogen groups to the TTF derivative **1** and succeeded in preparing n-type FETs based on them for the first time. We report here the synthesis, physical properties, and crystal structures of TTF derivatives and their FET characteristics. The relationship between the structure and FET behavior is also presented.

1. X = H
2. X = F
3. X = Cl
4. X = F
5. X = Cl
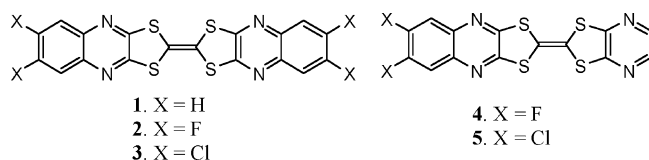
New TTF derivatives **2**−**5** were synthesized by a phosphite coupling reaction (see Supporting Information Scheme S1) and characterized by conventional chemical and physical methods. The oxidation potentials measured by differential pulse voltammetry (DPV) of **1**−**5** are 1.13, 1.53, 1.56, 1.43, and 1.44 V, respectively, from which the HOMO levels were calculated as shown in Table 1. Since their reduction potential could not be observed, the LUMO levels were estimated from the HOMO−LUMO energy gaps which were obtained from the absorption onset in the thin films (−3.27, −3.62, −3.81, −3.17, and −3.32 eV for **1**, **2**, **3**, **4**, and **5**, respectively). Introduction of halogen groups lowers the HOMO levels. It should be noted that the tetrahalogeno derivatives **2** and **3** exhibit considerably lower LUMO levels compared that of the dihalogeno derivatives **4** and **5**.

Table 1. Field-Effect Characteristics of Films **1**−**5** and the HOMO and LUMO Levels of These TTF Derivatives

compounds	HOMO (eV)[b]	LUMO (eV)[c]	mobility (cm²·V⁻¹·s⁻¹)	on/off ratio	V_{th} (V)
1[a]	−5.38	−3.27	0.20 (p)	1.0×10^6	−36
2	−5.83	−3.62	0.10 (n)	1.5×10^5	49
3	−5.84	−3.81	0.11 (n)	1.0×10^6	52
4	−5.70	−3.17	0.20 (p)	4.0×10^5	−50
5	−5.75	−3.32	0.64 (p)	3.3×10^5	−33

[a] From ref 6. [b] Estimated from the oxidation potentials; ferrocene used as internal standard. [c] Estimated from the HOMO and energy gaps.
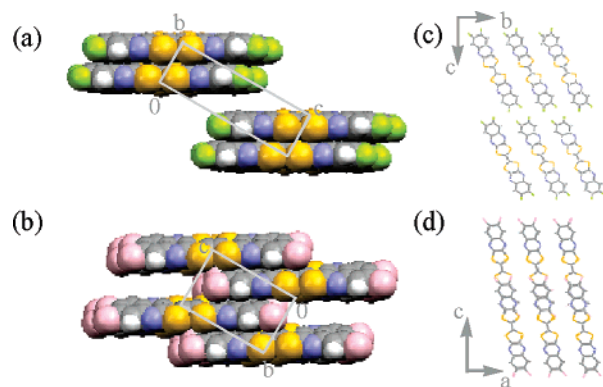
Figure 1. (a, b) Face-to-face π-stacking of compounds **2** and **3**. (c, d) View perpendicular to the long axis of the unit cell of **2** and **3**. (Yellow, blue, gray, white, green, and pink are sulfur, nitrogen, carbon, hydrogen, fluorine, and chlorine atoms, respectively.)

Single crystals of **2** and **3** were obtained by slow sublimation, and the crystal structures were determined by X-ray structure analysis. Molecules of **2** and **3** are completely planar and form face-to-face π-stacking, as shown in Figure 1. The molecule **2** affords a columnar structure, where the interplanar distance is 3.44 Å (Figure 1a). The 1,3-dithiole rings are overlapped with the pyrazine rings, suggesting the presence of intermolecular charge-transfer interactions between the donor and acceptor parts, which is similar to the molecular packing of **1**.[6] Interestingly, an intermolecular short S···S contact of 3.56 Å is observed between the columns to give a sheet-like network. In the crystal structure of **3** (Figure 1b), the molecules are stacked in a unique two-dimensional stacking manner (see Supporting Information), where the electron-withdrawing Cl substituents are sandwiched by the electron-donating TTF parts. The interplanar distance of 3.31 Å is shorter than that in **2**, and a short intermolecular S···S contact of 3.60 Å between the columns is also observed.

The FET devices were fabricated with top contact configuration. Gold electrodes were defined after 50 nm of semiconductor deposition by using shadow masks with W/L of 1.0 mm/200, 100,

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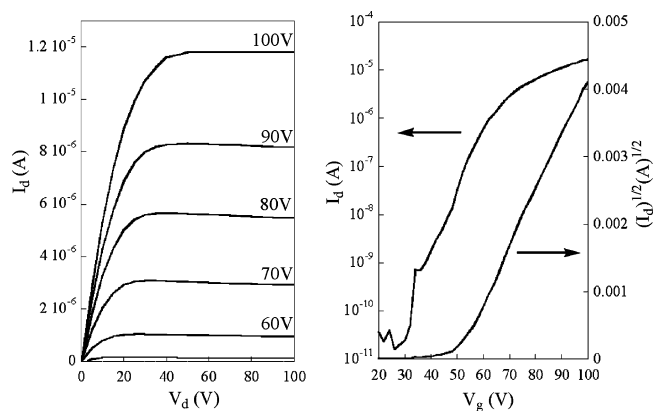‡ NHK Science and Technical Research Laboratories.

Figure 2. Drain current (I_d) versus drain voltage (V_d) characteristics for OFET of **3** (left), I_d and $I_d^{1/2}$ versus V_g plots at $V_d = 100$ V for the same device (right). The highest electron mobility calculated in the saturation regime is 0.11 cm²/V·s.

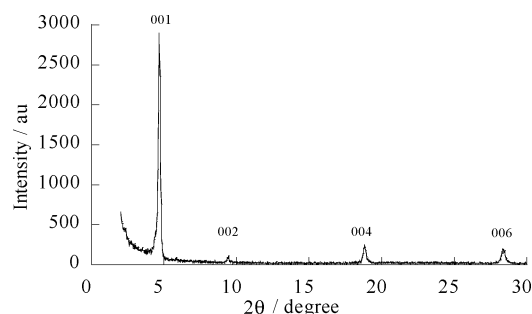**Figure 3.** X-ray diffraction of thin film deposited at room temperature of **2**.

50 μm. The SiO₂ gate electric was 200 nm thick and was treated with hexamethyldisilazane (HMDS), where the organic films were deposited at a rate of 0.3 Å/s at room temperature. The FET measurements were carried out at room temperature in a high vacuum chamber (10^{-5} Pa). The FET performances are summarized in Table 1. Tetrahalogeno derivatives **2** and **3** showed high electron mobilities and high on/off ratios, which are the first examples of n-type FETs using TTF derivatives. Figure 2 shows the drain current (I_d) versus voltage (V_d) characteristics for the FET device of **3**, where the electron mobility of **3** calculated in the saturation regime was 0.11 cm²·V⁻¹·s⁻¹. In contrast, dihalogeno derivatives **4** and **5** exhibited p-type characteristics with high hole mobilities. Particularly, **5** showed a high mobility of 0.64 cm²·V⁻¹·s⁻¹, which is the highest value reported so far in the thin film of TTF derivatives. This result shows that the difference in the number of halogen groups results in the dramatic effect on the FET behavior. This unusual behavior is rationalized in terms of frontier energy levels since the halogen groups change the HOMO and LUMO levels, as shown in Table 1. The chlorine derivatives showed slightly higher carrier mobilities in both n- and p-type FETs than did the corresponding fluorine derivatives. This may be attributed to the stronger intermolecular interactions in the chlorine derivatives.

The films of these TTF derivatives deposited on SiO₂/Si substrates were investigated by X-ray diffraction in reflection mode (XRD). In the thin film of **2**, sharp reflections up to the sixth order are observed (Figure 3). The strong intensity of the X-ray diffraction peaks indicates the formation of lamellar ordering and crystallinity on the substrate. The d spacing of **2** obtained from the first reflection peak is 1.87 nm, comparable to the molecular length obtained from the single-crystal X-ray analysis (1.82 nm), suggesting that the molecules are perpendicular to the substrate. However, the thin film

of **3** did not show clear XRD peaks. This may be attributed to the unique molecular stacking structure of **3**, where a molecular layer structure is not formed along the molecular long axis. The AFM image of the thin film of **3** exhibits small-size grains on the substrate (see Supporting Information). The dense packing might lead to the high electron mobility. On the other hand, sharp XRD peaks are observed in the films of **4** and **5** (see Supporting Information), where the d spacings are 1.73 and 1.83 nm, respectively. Compared with the calculated molecular lengths of these compounds (1.59 and 1.62 nm), molecules of **3** and **4** are considered to stand perpendicularly to the substrate.

In conclusion, four new TTF derivatives with halogeno-substituted quinoxaline rings were synthesized and characterized. The FET devices based on them showed excellent n- or p-type performances with high carrier mobilities. Introduction of halogen groups determined the FET polarity by controlling the HOMO and LUMO levels of the molecules.

Supporting Information Available: Synthesis, absorption spectra, DPVs, I_d versus V_d and I_d versus V_g characteristics for **2**, **4**, and **5**, X-ray crystallographic data for **2** and **3** in CIF format, and AFM of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (b) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900. (c) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (d) Moon, H.; Zeis, R.; Borkent, E. J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322.

(2) (a) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33. (b) Facchetti, A.; Letizia, J.; Yoon, M.-H.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Chem. Mater.* **2004**, *16*, 4715. (c) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044.

(3) (a) Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812. (b) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986. (c) Tulevski, G. S.; Miao, Q.; Afzali, A.; Graham, T. O.; Kagan, C. R.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1788.

(4) (a) Mas-Torrent, M.; Durkut, M.; Hadley, P.; Ribas, X.; Rovira, C. *J. Am. Chem. Soc.* **2004**, *126*, 984. (b) Mas-Torrent, M.; Hadley, P.; Bromley, S. T.; Crivillers, N.; Veciana, J.; Rovira, C. *Appl. Phys. Lett.* **2005**, *86*, 012110.

(5) (a) Noda, B.; Katsuhara, M.; Aoyagi, I.; Mori, T.; Taguchi, T.; Kambayashi, T.; Ishikawa, K.; Takezoe, H. *Chem. Lett.* **2005**, *34*, 392. (b) Katsuhara, M.; Aoyagi, I.; Nakajima, H.; Mori, T.; Kambayashi, T.; Ofuji, M.; Takanishi, Y.; Ishikawa, K.; Takezoe, H.; Hosono, H. *Synth. Met.* **2005**, *149*, 219.

(6) Naraso; Nishida, J.; Ando, S.; Yamaguchi, J.; Itaka, K.; Koinuma, H.; Tada, H.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 10142.

(7) (a) Mushrush, M.; Facchetti, A.; Lefenfeld, M.; Katz, H. E.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 9414. (b) Klauk, H.; Halik, M.; Zschieschang, U.; Eder, F.; Schmid, G.; Dehm, C. *Appl. Phys. Lett.* **2003**, *82*, 4175. (c) Katz, H. E.; Hong, X. M.; Dodabalapur, A.; Sarpeshkar, R. *J. Appl. Phys.* **2002**, *91*, 1572.

(8) (a) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138. (b) Yoon, M.-H.; DiBenedetto, S. A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 1348.

(9) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Brédas, J.-L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16,* 4436.

(10) (a) Facchetti, A.; Deng, Y.; Wang, A.; Koide, Y.; Sirringhaus, H.; Marks, T. J.; Friend, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4547. (b) Letizia, J. A.; Facchetti, A.; Stern, C. L.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 13476. (c) Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996.

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