

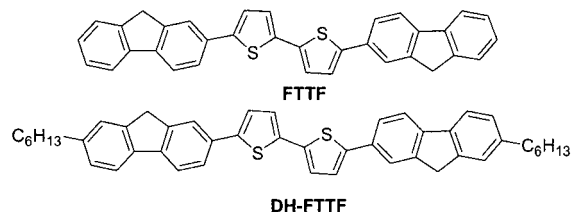
High Field-Effect Mobility Oligofluorene Derivatives with High Environmental Stability

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Organic and polymeric semiconductor-based thin-film field-effect transistors (OFETs) are of great interest for low-cost large-area memories and driving circuits in display applications.¹ In these organic devices, the charge carrier transport is dominated by the hopping mechanism at room temperature.² Therefore, highly ordered thin films with large interconnected polycrystalline grains are necessary to obtain high mobilities.³ To date, only a



Chemical structures of oligofluorene derivatives.

limited number of organic semiconductors can reach mobilities similar to those of α -Si transistors.⁴ Most *p*-channel organic semiconductors have been based on thiophene-derivatized oligomers and polymers.⁵ There are a few other systems relying on aromatic macrocyclics, such as metallophthalocyanines, and fused aromatic rings, such as pentacene and tetracene.^{4a,5} Few other types of conjugated systems have been explored thus far. In addition, most of the reported *p*-channel semiconductors have relatively low band gaps and high HOMO levels. Therefore, they tend to be easily photooxidized and cause degradation of the resulting devices.

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(1) (a) Crone, B.; Dodabalapur, A.; Lin, Y. Y.; Filas, R. W.; Bao, Z.; Sarpeshkar, R.; Katz, H. E.; Li, W. *Nature* **2000**, *403*, 521–523. (b) Gelincik, G. H.; Geuns, T. C. T.; de Leeuw, D. M. *Appl. Phys. Lett.* **2000**, *77*, 1487–1489. (c) Klauk, H.; Jackson, T. N. *Solid State Technol.* **2000**, *43*, 63. (d) Rogers, J. A.; Bao, Z.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Katz, H. E.; Kuck, V.; Ammundson, K.; J.; Drzaic, P. *Proc. Natl. Acad. Eng.* **2001**, *98*, 4817–5370. (e) Dimitrakopoulos, C. D.; Mascaro, D. J. *IBM J. Res. Dev.* **2001**, *45*, 11–28.

(2) (a) Katz, H. E.; Bao, Z. *J. Phys. Chem. B* **2000**, *104*, 671–678. (b) Horowitz, G.; Hajlaoui, M. E. *Adv. Mater.* **2000**, *12*, 1046–1050.

(3) Bao, Z.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 42–44.

(4) (a) Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Trans. Elec. Dev.* **1997**, *44*, 1325. (b) Li, X. C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206–2207. (c) Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chem. Mater.* **1998**, *10*, 457. (d) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664–672. (e) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741–1744. (f) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478–481.

(5) Katz, H. E.; Bao, Z.; Gilat, S. *Acc. Chem. Rev.* **2001**, *34*, 359–369.

In this contribution, we report high-performance OFETs using two new oligomers, based on fluorene and bithiophene, as the semiconducting layer. Very high field-effect mobility (greater than 0.1 cm²/Vs) has been achieved with **DH-FTTF**. More importantly, these semiconductors exhibit high on/off ratios and no decrease in the on/off ratios for more than two months in air with exposure to ambient light. Fluorene-containing polymers have been previously reported for light-emitting diodes and transistors.⁶ High mobility was obtained only when these liquid crystalline (LC) polymers were annealed in their LC phase aligned with a rubbed polyimide surface to form a monocrystalline domain.^{6c} In contrast to the oligofluorenes used for light-emitting diodes, our oligomers are not substituted at the methylene linkage fusing the two benzene rings (9-position of fluorene) to facilitate π - π stacking in these oligomers. The **FTTF** and **DH-FTTF** were synthesized using the Suzuki coupling reaction between 5,5'-dibromo-2,2'-bithiophene and the corresponding pinacolato boronic ester-substituted fluorene and 2-hexylfluorene.^{6b} The resulting oligomers were purified by repeated washing with hot chloroform followed by vacuum sublimation to yield bright yellow powders. The elemental analysis results matched closely to the calculated values. The UV-vis absorption spectra of **FTTF** and **DH-FTTF** thin films prepared by vacuum deposition (\sim 50 nm thick) are very similar with the maximum absorption at ca. 350 nm corresponding to the π - π^* transition.

X-ray diffraction analyses were performed on films vacuum-deposited onto Si/SiO₂ substrates. All films are highly ordered as evidenced by the fact that sharp diffraction peaks, extending in some cases to the eighth order, were observed. For unsubstituted **FTTF**, the separation (24 Å) between layers calculated from the primary X-ray peak is almost the same as its extended length, indicating that the molecules adopt an edge-on orientation similar to that of other conjugated oligomers.⁷ This type of orientation has been found particularly useful in achieving high mobilities since the π - π stacking direction is in the plane of the current-flowing direction. The dihexyl-substituted oligomers also appear to adopt the edge-on orientation but with the chains somewhat inclined since the layer separation of ca. 34 Å, similar to dihexyl α -hexathienyl,⁸ is shorter than the extended molecular length. **FTTF** showed a substantial amorphous component for the thin film deposited with the substrate held at room temperature. However, this amorphous component disappeared at elevated substrate temperatures together with increased diffraction peak intensities, which indicates improved ordering.

All of the oligomers were used as *p*-type transistors and are accumulation devices. Figure 1 shows the typical drain-source current (I_{DS}) characteristics of FETs with **FTTF** and **DH-FTTF** deposited at elevated substrate temperatures with different gate voltages. It is seen that the drain-source current scales up with increasing gate voltages (V_G). The field-effect mobilities were calculated using the I_{DS} values in the saturation regions, and the results for all oligomers obtained at different T_D are summarized in Table 1.⁹ The mobilities depend strongly on both the deposition conditions and the device geometry. It has been previously

(6) (a) Klärner, G.; Davey, M. H.; Chen, W. D.; Scott, J. C.; Miller, R. D. *Adv. Mater.* **1998**, *10*, 993. (b) Woo, E. P.; Shiang, W. R.; Inbasekaran, M.; Roof, G. R. U.S. Patent 5,962,631, 1999. (c) Belletete, M.; Ranger, M.; Beaupre, S.; Leclerc, M.; Durocher, G. *Chem. Phys. Lett.* **2000**, *316*, 101–107. (d) Advincula, R.; Xia, C.; Inaoka, S. *Polym. Prepr.* **2000**, *41*, 846–847. (e) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. *Appl. Phys. Lett.* **2000**, *77*, 406–408.

(7) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716–8721.

(8) Katz, H. E.; Laquindanum, J. G.; Lovinger, A. J. *Chem. Mater.* **1998**, *10*, 633–638.

(9) Sze, S. M. *Semiconductor Devices: Physics and Technology*; Wiley: New York, 1985.

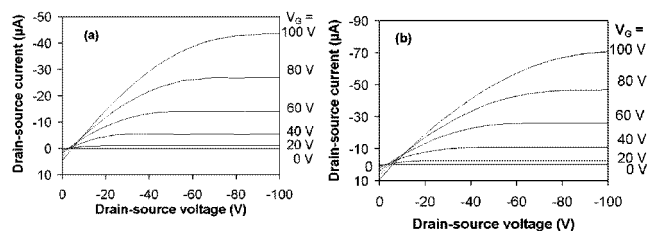


Figure 1. I_{DS} vs V_{DS} characteristic of (a) FTTF (100 °C) and (b) DH-FTTF (140 °C) at different gate voltages prepared at elevated substrate temperatures, with channel length $L = 280 \mu\text{m}$ and channel width $W = 4 \text{ mm}$.

Table 1. Field-Effect Mobilities of FTTF and DH-FTTF Transistors Prepared at Different Substrate Temperatures (T_D) Using Top-Contact Geometry

T_D (°C)	FTTF		DH-FTTF	
	mobility (cm^2/Vs)	on/off ratio	mobility (cm^2/Vs)	on/off ratio
25	0.02–0.03	10^5 – 10^6	0.02–0.03	2×10^3
80	0.03	2000	0.04	6×10^3
100	0.07–0.08	9000 – 10^4	0.05–0.06	2×10^3
120	0.04–0.05	8000 – 10^4	0.04–0.06	10^4 – 10^5
140	0.04–0.05	1000–2000	0.094–0.11	10^4 – 10^5

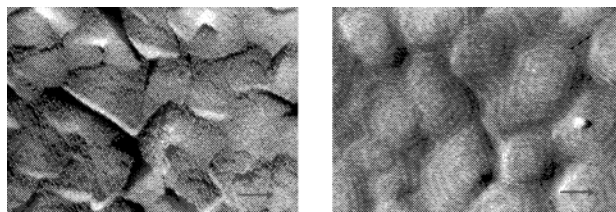


Figure 2. Transmission electron micrographs of thin films from (a) FTTF, $T_D = 100 \text{ °C}$ and (b) DH-FTTF, $T_D = 140 \text{ °C}$.

reported that the mobility of most organic semiconductors strongly depends on the T_D .³ Similar trends are found with these fluorene-containing oligomers.

In general, the field-effect mobility increases with increasing T_D , which is attributed to better ordered thin films and larger grain sizes at elevated T_D . Indeed, X-ray diffraction patterns showed higher diffraction intensity for thin films of the same thickness deposited at higher T_D . The transmission electron micrographs also showed sharper grain boundaries and larger crystal sizes for higher T_D thin films. For example, the grain sizes for FTTF and DH-FTTF were both on the order of 20–50 nm at $T_D = 25 \text{ °C}$. The grain sizes became much bigger at elevated T_D , on the order of 200–500 nm (Figure 2).

It was found that the mobilities of these oligomeric devices prepared using the bottom contact geometry (drain and source electrodes deposited above the dielectric layer and under the semiconducting layer) always tend to be lower than those using the top contact geometry (drain and source electrodes deposited on top of the semiconducting layer). Similar observations have been reported for pentacene and some n -channel materials.¹⁰ This was attributed to the small charge injection areas and poor wetting of organic semiconductor vapor to the electrodes in the bottom

contact geometry. This problem can be partially or completely solved by surface treatment of the Au electrodes with thiol monolayers.¹⁰ Such studies with our oligomers are in progress.

The best mobility thus far is achieved with DH-FTTF at a substrate temperature of 140 °C, which is on the same order of magnitude as α -Si transistors. This value may be further improved by surface modification of the dielectric and contact electrodes.^{4a} The thin film deposited at this temperature was examined by transmission electron microscope and found to exhibit densely packed 200–500 nm grains with extensive multilayer terraces and screw dislocations, which indicated high crystallinity and three-dimensional order (Figure 2b). Synthesis of other oligofluorene derivatives is underway. Preliminary results indicated that the mobility of terfluorene is on the order of $10^{-2} \text{ cm}^2/\text{Vs}$.

The on/off ratios of the oligomers are quite high (more than 1000 in most cases and more than 10^5 for FTTF at room temperature) without any special optimization effort. Careful purification of the semiconducting materials, surface treatment of the dielectric surface, and patterning of the semiconducting layer may lead to improved on/off ratios. The OFETs made from these two oligomers also show improved oxidative stability. No decrease in on/off ratio and mobility have been observed even after the transistors have been exposed to ambient light and air in a synthetic lab for more than 2 months. Thin films of DH-FTTF showed no decrease in the peak intensity at the maximum UV absorption wavelength after being irradiated with a UV lamp (366 nm, 60 Hz, 0.16 amps) for 48 h. In addition, no carbonyl formation was observed in the FTIR spectrum for the irradiated film. Many other high mobility organic semiconductors usually start to exhibit decreased on/off ratio hours after exposure under air and ambient light. The improved stability is extremely valuable for realizing long-lived organic electronic devices.

In summary, high-performance oligofluorene derivatives have been synthesized and used as the semiconducting materials for OFETs. These oligomers showed p -channel transistor behavior with the best mobilities in the same order of magnitude as α -Si devices. In addition to the improved oxidative stability, DH-FTTF was also found to be relatively soluble (more than 1 mg/mL) in warm chlorobenzene. Preliminary results indicate that OFETs can also be fabricated by casting from solution with mobilities in the order of $10^{-3} \text{ cm}^2/\text{Vs}$. These new high-performance and stable organic semiconductors will be extremely valuable for the future commercialization of organic electronic devices.

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Supporting Information Available: (1) Experimental procedures (2) UV-vis and FT-IR spectra of DHFTTF; (3) X-ray diffraction spectrum of FTTF (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(10) (a)Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. J. *J. Am. Chem. Soc.* **2000**, *122*, 7787–7792. (b) Dimitrakopoulos, C. D. Personal communication.