

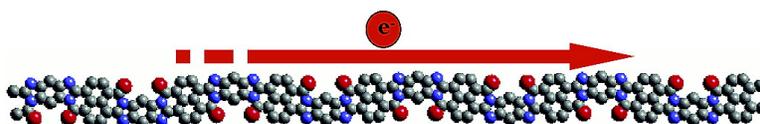
Communication

High Electron Mobility in Ladder Polymer Field-Effect Transistors

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High Electron Mobility in Ladder Polymer Field-Effect Transistors

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Charge transport of both holes and electrons in conjugated polymer semiconductors is important for the device applications of the materials in light-emitting diodes, photovoltaic cells, and thin film transistors. Much progress has been made in developing p-type conjugated polymers in the past two decades, leading to the recent achievement of high field-effect mobility of holes ($0.05\text{--}0.1\text{ cm}^2/(\text{V s})$) in solution-cast regioregular poly(3-hexylthiophene) thin films.¹ Development of n-type conjugated polymer semiconductors capable of electron transport in field-effect transistors (FETs) has heretofore lagged far behind that of p-type polymers.²⁻⁴ Although a number of n-type organic molecules and oligomers with high electron mobilities have recently been reported,² achievement of high electron mobility in conjugated polymers remains an important goal for the realization of high performance plastic electronics. Because charge carriers in conjugated polymers, described as “holes” and “electrons”, are strictly radical cations (or positive polarons) and radical anions (or negative polarons), respectively, their injection and transport are facilitated by low ionization potential and high electron affinity.^{1,2} Although π -conjugated heterochain polymers such as the polyquinolines, polyquinoxalines, polyanthrazolines, and polybenzobisazoles are known to have reversible electrochemical reduction and electron-accepting properties,³ none of these has sufficiently high electron affinity essential for facile electron injection and transport in the presence of oxygen and water in air and thus for achievement of air-stable n-channel polymer field-effect transistors.

We report herein the observation of field-effect electron mobilities as high as $0.1\text{ cm}^2/(\text{V s})$ in a solution spin-coated conjugated ladder polymer, poly(benzobisimidazobenzophenanthroline) (BBL). These electron mobilities are the highest observed to date in a conjugated polymer semiconductor. Furthermore, the field-effect mobility of electrons is several orders of magnitude enhanced in BBL with a ladder architecture as compared to its nonladder conjugated polymer derivative BBB (Figure 1).

The double-stranded (ladder) polymer BBL and its nonladder derivative BBB have unusually high glass transition temperatures ($>500\text{ }^\circ\text{C}$) and high thermal stability in air. The rich nitrogen and oxygen heteroatoms in both polymers give rise to excellent electron-accepting properties, including reversible n-type doping to high dc conductivity, the ability to accept up to 2 electrons per the repeat unit of Figure 1, and a high electron affinity of ca. $4.0\text{--}4.4\text{ eV}$.⁵ However, prior studies of charge transport in BBL thin films prepared from Lewis acid (AlCl_3 , GaCl_3 , FeCl_3)/nitromethane solutions⁶ found rather low electron mobility ($10^{-6}\text{--}10^{-4}\text{ cm}^2/(\text{V s})$).^{4a,b} Electron diffraction studies showed that BBL thin films prepared from methanesulfonic acid (MSA) had a larger degree of crystallinity than those from Lewis acid solutions. Here, we fabricated and studied insulated gate FETs based on the ladder BBL and nonladder BBB from their MSA solutions. BBL thin films were spin coated from a ca. 0.1 wt. % solution in MSA. The resulting BBL thin films were immersed in deionized water to remove any remaining MSA solvent and to facilitate aggregation and crystal-

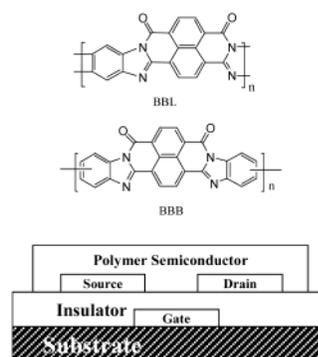


Figure 1. The molecular structures of ladder BBL and nonladder BBB polymer semiconductors and schematic of the polymer field-effect transistor. The source and drain electrodes were gold.

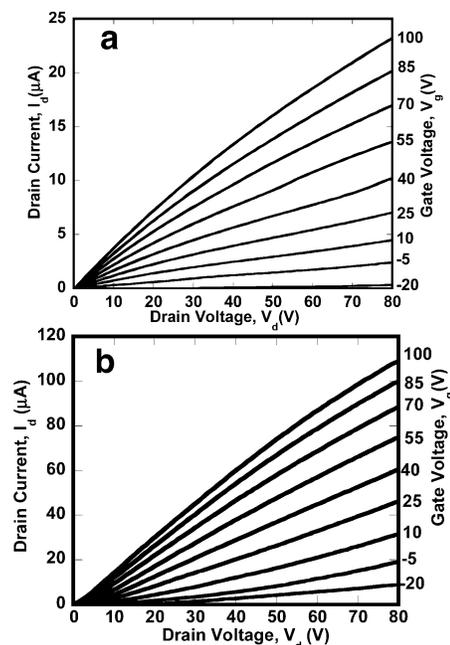


Figure 2. Output characteristics of BBL FETs with $\mu_{e,\text{sat}} = 0.03\text{ cm}^2/(\text{V s})$ (a) and $\mu_{e,\text{lin}} = 0.1\text{ cm}^2/(\text{V s})$ at $V_d = 10\text{ V}$ (b).

lization.^{7,8} All of the devices were dried in an oven at $70\text{ }^\circ\text{C}$ overnight (12–16 h) after removal from water. Prior to electrical testing of some of the devices, annealing in air or vacuum at different temperatures ($100\text{--}200\text{ }^\circ\text{C}$) for different times was done. We measured the electrical characteristics of all of the thin film transistors in ambient air at room temperature.

The devices did not show p-channel characteristics. Instead, typical n-channel FET output characteristics were observed as exemplified in Figure 2. We calculated the field-effect mobility of electrons (μ_e) by using the saturation region transistor equation,^{2b} $I_d = (W/2L)\mu_e C_o (V_g - V_t)^2$, where I_d is the source-drain current, V_g is the gate voltage, C_o is the capacitance per unit area of the

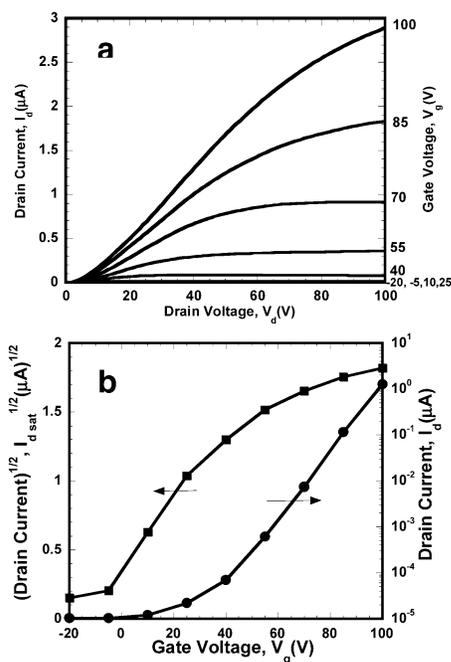


Figure 3. Output (a) and transfer (b) characteristics of a BBL FET with $W = 400 \mu\text{m}$, $L = 20 \mu\text{m}$, and $\mu_{e,\text{sat}} = 0.03 \text{ cm}^2/(\text{V s})$.

dielectric (SiO_2 , $11 \text{ nF}/\text{cm}^2$ for the 300-nm thickness) layer, and V_t is the threshold voltage. BBL FETs annealed at $100 \text{ }^\circ\text{C}$ for 5 min gave a maximum $\mu_{e,\text{sat}}$ value of $0.05 \text{ cm}^2/(\text{V s})$. A longer annealing period of the same device at $100 \text{ }^\circ\text{C}$ resulted in an electron mobility of $0.03 \text{ cm}^2/(\text{V s})$ and an on/off current ratio of 2×10^3 . The highest electron mobility in BBL FETs, $0.1 \text{ cm}^2/(\text{V s})$ calculated using linear region approximation^{2b} at $V_d = 10 \text{ V}$, was observed for a device (channel width $W = 500 \mu\text{m}$, channel length $L = 25 \mu\text{m}$) in which a siloxane compound, 1,1,1,3,3,3-hexamethyldisilazane, was vapor deposited on top of SiO_2 to promote better adhesion of the spin-coated BBL thin film (Figure 2b).

Excellent saturation of the drain current was observed in the electrical properties of a BBL FET ($W = 400$ and $L = 20 \mu\text{m}$) after annealing for 5 min in a vacuum at $105 \text{ }^\circ\text{C}$ (Figure 3). The maximum electron mobility of this device was $0.03 \text{ cm}^2/(\text{V s})$, and the maximum on/off current ratio was 5×10^5 . Annealing in a vacuum at $105 \text{ }^\circ\text{C}$ for various periods up to 115 min resulted in no change in the mobility. However, the on/off current ratio was gradually reduced to 10^3 . In light of these results, we systematically investigated the effects of the annealing temperature and time on the performance of the BBL thin film transistors. We found that annealing at $100\text{--}125 \text{ }^\circ\text{C}$ for 10–30 min appeared to be optimum for achieving high mobility with high on/off current ratios. Longer annealing times at these temperatures had the main effect of reducing the on/off current ratio as a result of increased off current. Higher annealing temperatures ($130\text{--}200 \text{ }^\circ\text{C}$) also primarily reduced the FET current modulation. These effects of annealing temperature and time on the performance of BBL thin film transistors are related to changes in the morphology of the ladder polymer films.

Comparative studies of n-channel FETs made from the structurally related nonladder BBB and using similar solution processing of thin films gave a maximum electron mobility of $10^{-6} \text{ cm}^2/(\text{V s})$. A series of binary blends of BBB and BBL similarly resulted in low field-effect mobilities of the order $10^{-5} \text{ cm}^2/(\text{V s})$ (Supporting Information). This finding of several orders of magnitude higher electron mobility in the ladder architecture as compared to the otherwise similar but nonladder conjugated polymer may seem surprising. It is generally assumed that a conjugated ladder polymer

would have better π -electron delocalization and thus also would have better electronic properties including charge carrier mobility.^{5–7} However, the reason for the observed large difference in electron mobility may not be just because of better π -electron delocalization in the ladder structure as previously thought.^{5–7} Both BBL and BBB have identical optical band gap ($E_g = 1.8 \text{ eV}$) and absorption spectra, electron affinity ($\text{EA} = \text{ca. } 4.0\text{--}4.4 \text{ eV}$) and redox properties, and dc conductivity when chemically doped.^{5–7} We find the major difference between the two polymers is morphology; BBL films, spin coated or cast from MSA solutions, were revealed by X-ray and electron diffraction to be semicrystalline,^{7c,8} whereas BBB films were completely amorphous. AFM images of BBL thin films revealed nanoscale sheets that are randomly oriented within the film (Supporting Information). The observed large enhancement of carrier mobility by the ladder architecture of BBL is thus due to the more efficient π -stacking and greater intermolecular order, leading to a more crystalline ladder polymer solid film.

In summary, field-effect mobility of electrons as high as $0.1 \text{ cm}^2/(\text{V s})$ has been realized in the ladder polymer BBL, thus demonstrating that electron transport can be as facile as hole transport¹ in conjugated polymer semiconductors. The finding that carrier mobility in BBL with ladder architecture is about 10^5 enhanced as compared to its nonladder analogue BBB is instructive in tailoring intermolecular π -interactions for maximizing electron transport. In the search for polymer semiconductors with higher charge carrier mobilities, π -conjugated ladder polymers offer good prospects because of their unique structural features that provide a bridge between strictly 1D conjugated polymers and two-dimensional (2D) graphite sheets which have an in-plane carrier mobility of $1.5 \times 10^4 \text{ cm}^2/(\text{V s})$ at room temperature.⁹

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Supporting Information Available: Experimental procedures and additional data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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