High Mobility Single-Crystal OTFTs based on TIPS Anthracene Derivatives

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Abstract

We elucidated a way to increase the mobility of π-stacked materials by comparing various single-crystal OFETs. A high field-effect mobility (of 3.7 cm^2/Vs) was obtained by increasing the effective π-stacking area and decreasing the π-stacking distance.

1. Introduction

For recent decades, organic semiconductors based on polymers, oligomers, and small molecules have been sufficient to rival and alter to inorganic semiconductors due to diverse applications of theirs. Especially, organic semiconductors have been considered as active materials for organic light emitting diode(OLED) and OTFT fields (e.g., switching devices for flexible display panel, low-cost memory cards and smart price tags and labels, spin coating, inkjet printing, etc). Recent works have shown that a well-defined single-crystalline microstructure and a good electrical OFET performance can be obtained by means of simple solution process involving soluble organic semiconductors. Field-effect mobilities as high as 1.4 cm^2/Vs were reported by Mas-Torrent and co-workers[1] for OFETs composed of single-crystalline dithiotetrathiafulvalene (DT-TTF). Cho and co-workers reported solution-processed single-crystalline nanowire transistors, based on poly-3-hexylthiophene[2] and triisopropylsilylethynyl (TIPS) pentacene,[3] with field-effect mobilities above 0.1 cm^2/Vs. However, since most of the works on single-crystal OFETs have focused on enhancing the device performance, the effect of molecular packing in π-stacked organic single crystals on the quality of the devices has not been thoroughly studied to date. Mas-Torrent and co-workers tried to explain the differences observed in the field-effect mobilities of single-crystal OFETs composed of various DT-TTF derivatives by classifying them into three different structural groups, namely, herringbone, π-stacking, and edge-to-face dimer stacking groups. Herein, we investigated the properties of new soluble oligomeric OTFT materials that contain 9,10-bis(triisopropylsilylethynyl) anthracene (TIPSAN) derivatives. The single crystal OTFTs exhibited high hole mobility (3.7 cm^2/Vs) by increasing the effective π-stacking area and decreasing the π-stacking distance.

2. Experimental

*Single-Crystal Field-Effect Transistor*s: Bottom-gate, top-contact devices were fabricated. The SiO_2 dielectric was treated with HMDS (Aldrich), via spin coating, and baked for 20 min in an oven at 60°C. To minimize air contact and guarantee sufficient evaporation of the solvent, the single crystals were fabricated in a closed jar filled with Ar gas. Toluene and chlorobenzene were used as the solvents (at concentrations between 0.02 and 0.5 wt%). The heated solution (at 60°C) was poured onto the HMDS-treated dielectric and allowed to evaporate very slowly in the closed jar for about five hours. The well-defined single crystals thus obtained were dried in a vacuum chamber for 24 hours. The source and drain electrodes were then deposited onto the single-crystal layer by means of the thermal evaporation of gold through shadow masks. The channel lengths (*L*) were 50–150 μm. The electrical characteristics of the FETs were measured in air using Keithley 2400 and 236 source/measure units.

Characterization: The morphologies of the single-crystal rods were characterized by means of optical microscopy (OM), POM (Axioplan, Zeiss), FE-SEM (Hitachi S-4200, with an accelerating voltage of 8 kV), and contact-mode atomic force microscopy (AFM, Multimode IIIa, Digital Instruments).

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3. Results and discussion

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The Suzuki coupling reactions of TIPSAN dibromide with mono-borate of bithiophene, mono-borate of naphthalene, and mono-borate of anthracene were carried out to produce TIPSAN-BT, TIPSAN-NA, and TIPSAN-AN, respectively, in yields in the range 80~86 %. The obtained TIPSAN derivatives were purified with chromatography, recrystallization, and then sublimation, and characterized with NMR, IR, mass spectroscopy and elemental analysis. The obtained TIPSAN derivatives were bright purple highly crystalline solids. TIPSAN-BT showed good solubility in common organic solvents, on the other hand, TIPSAN-NA was soluble in hot solvent and TIPSAN-AN showed low solubility in common solvent even though TIPSA derivatives have bulky TIPS group.

Single crystals of various TIPSAN derivatives were easily grown from toluene and hexane for the X-ray crystallography studies. All these single crystals were found to form triclinic structures. Out-of-plane X-ray diffraction (XRD) experiments were also performed to check the arrangement of the TIPSAN-derivative molecules in single-crystal microrods formed on an HMDS-treated SiO_2 substrate. We found that the peak positions in the out-of-plane profile of TIPSAntBT correspond to the (00l) or c direction when compared with the profile of a crystallographic powder pattern. Single-crystal OFET devices based on the TIPSAnt derivatives were fabricated by means of gold evaporation through a shadow mask on the single-crystal microrods grown on the HMDS-treated SiO_2 dielectric (using heavily doped Si as the gate electrode). The devices were tested at room temperature in air and a dark environment. The transfer and output characteristics of these single-crystal OFETs are shown in Figure 1. The transfer properties of the devices were measured in the saturation regime at gate-voltage (VG) values between 20 and -100 V and a constant drain voltage (VD) of -100 V.

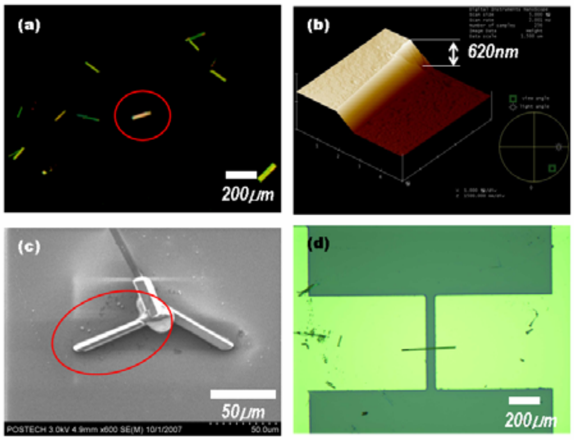

Figure 1. Morphological characterization of single-crystal **TIPSAntBT**: (a) polarized optical microscopy, (b) atomic force microscopy, (c) scanning electron microscopy, and (d) optical microscopy image with device structure.

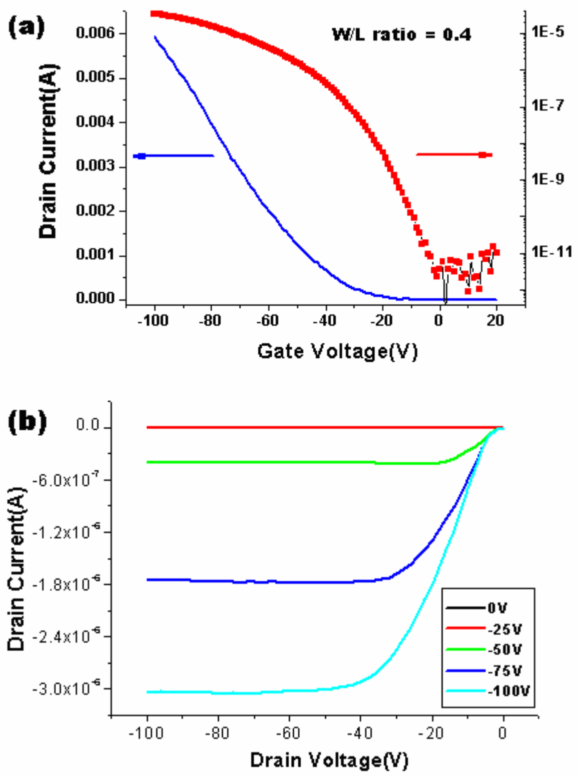

Figure 2. OTFT characteristics of TIPSAN-NA

The single-crystal OFETs fabricated using TIPSAN-NA showed the best electrical performance, with an average field-effect mobility of 1.82 cm2/Vs (the highest mobility was 3.7 cm2/Vs). To the best of our knowledge, this is the highest field-effect mobility reported so far for solution-processed single-crystal OFETs.

4. Summary

Single crystal derivatives exhibited mobility as high as 3.7 cm^2/Vs, I_{on}/I_{off} current ratio of 10^4, threshold voltage of -40 V, and subthreshold slop of 14 V/dec, respectively. In the crystal structure, TIPSAN derivatives showed large π -stacking area of core and end groups with short π-π stacking distance of 3.525 ~ 3.485 Å.

5. Acknowledgements

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6. References

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