TIPS Anthracene Derivatives for Solution Process OTFT Materials : Large π-stacking area and Easy Crystallizability

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Abstract

A series of new channel materials using triisopropylsilylethynyl anthracene(TIPSAN) derivatives are synthesized by well known reaction. The TIPSAN derivatives exhibit an excellent field-effect mobility with hole mobility as high as 0.1 cm2V-1s-1 by solution-process and slip stack structure of core and end groups with short π-π stacking distance of 3.525 ~ 3.485 Å by single crystal structures.

1. Introduction

Organic thin film transistors (OTFTs) are low-cost organic electronic devices, with a simple structure, and can be used in large-area electronic applications. The OTFTs with the best overall reported performance are based on the organic semiconductor pentacene a high carrier field effect mobility >1 cm^2/Vs has been achieved with a by vacuum deposition process.[1-4] However vacuum deposition is expensive, which makes the potential of organic electronics difficult to realize. Solution processed organic semiconductors have attracted considerable interest because of the very low costs of deposition processes such as ink jet printing, spin-casting, and dipping.[5,6] They also have higher compatibility with plastic substrates than silicon based thin film transistor (TFT), and diverse potential applications, such as in driving circuits of large-area flexible display panels, new generation smart cards, integrated logic circuits, and sensors etc. Herein, we investigated the properties of new soluble oligomeric OTFT materials that contain 9,10-bis(triisopropylsilylethynyl) anthracene (TIPSAN) derivatives. The introduction of 2,6-substituents in the anthracene core is expected to give the more extended π-conjugation due to enhanced intermolecular overlap of π-π systems in the solid state and the higher planarity. The anthracene cores with bulky TIPS groups are expected to affect the solubility, oxidation stability and packing ability of these newly designed oligomers, and the fused small aromatic side units are expected to result in increased mobility due to extended π-conjugation and enhanced intermolecular overlap.

2. Experimental

TFT Fabrication: OTFTs were fabricated using the three functionalized anthracene derivatives as the active layer. A highly n-doped silicon wafer was used as a substrate and gate electrode. A 300 nm thick thermally grown SiO_2 was used as the gate dielectric layer. Substrates were modified with silylating agent octyltrichlorosilane (OTS) from 10-mM solutions in toluene for 2 h at room temperature. Films of organic semiconductor were spin coated at 2000 rpm for 60s from 0.7 wt% chloroform solution, with normal thickness 60 nm. Source and drain contacts were

deposited on top of the active layer by evaporating gold through a shadow mask. For all measurements, we used channel lengths (L) of 150 ㎛ and channel widths (W) of 1500 ㎛. Electrical characteristics of the FETs were measured in air using both Keithley 236 source/measure units. Field-effect mobilities were extracted in the saturation regime from the drain current versus gate-source voltage characteristics at a drain-source voltage of - 60 V.

Instruments: Melting points were determined using an Electrothermal Mode 1307 digital analyzer. ^{1}H-NMR spectral data were expressed in ppm relative to the internal standard and were measured on a DRX 300 MHz NMR spectrometer. FT-IR spectra were recorded with a Bomem Michelson series FT-IR spectrometer and the UV-visible absorption spectra were recorded in chloroform on a Shimadzu UV-3100 spectrophotometer. Elemental analyses were performed by Leco Co. CHNS-932. TGA measurments were performed on a Perkin-Elmer Series 7 analysis system under N_2 at a heating rate of 10 ℃/min. Cyclic voltammetry measurements of the polymer films were performed on a BAS 100 B/W electrochemical analyzer in acetonitrile with 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) as the supporting electrolyte at a scan rate of 100 mV/s. The potentials were measured against an Ag/AgCl reference electrode with ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. AFM (Multimode IIIa, Digital Instruments) operating in tapping-mode was used to image surface morphology of our functionalized anthracene derivative semiconductors. Synchrotron X-ray diffraction analysis for semiconductor film was performed at 10C1 beam line (wavelength ~ 1.54 Å) at Pohang Accelerator Laboratory (PAL). For grazing incidence X-ray scattering (GIXD), the films were illuminated at a constant incidence angle of 0.15°.

3. Results and discussion

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. The TIPSAN derivatives were found to be stable up to 420 ℃ with TGA. The highest occupied molecular orbital (HOMO) levels of TIPSAN derivatives were estimated to be 5.11 ~ 5.47 eV, respectively. On the basis of these results, it is supposed that the oxidation stabilities of the oligomers are higher than that of TIPS pentacene (5.20 eV), so result in better device stability. We studied the organic thin film transistor properties of the TIPSAN derivatives in OTFTs with a top-contact OTFT device configuration built on n-doped silicon wafers with a 300 nm thick thermally grown SiO_2 dielectric layer. Two types of substrate were prepared, bare SiO_2 (no surface treatment) and octyltrichlorosilane (OTS) treated SiO_2. Films of the organic semiconductors were spin coated with a nominal thickness of 60 nm. In all these measurements, we used channel lengths (L) of 150 ㎛ and channel widths (W) of 1500 ㎛.

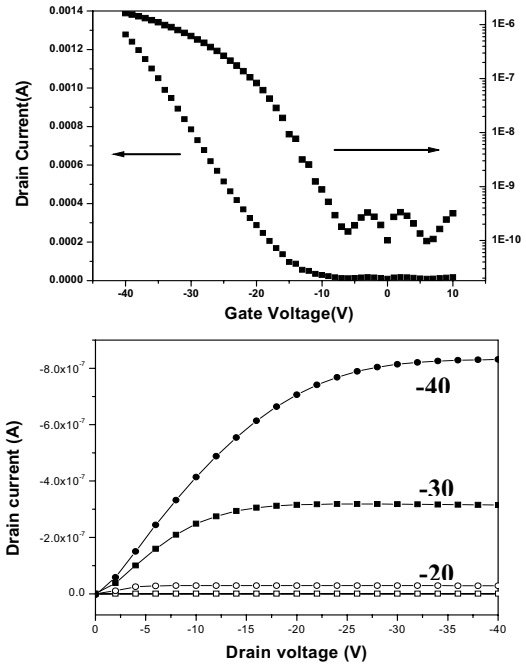

Fig. 1. OTFT characteristics of TIPSAN derivative

At a given negative gate voltage, I_{ds} initially increased linearly with a small negative V_{ds} and then saturates due to a pinch off of accumulation layer at the interface between semiconductor and gate insulator. Fig. 1 showed transfer characteristic curves of OTFTs fabricated with TIPSAN derivative, respectively, where gate voltage (V_{gs}) was swept from 10V to -40V and V_{ds} was set at -40V. The OTFTs with TIPSAN derivative deposited by spin coating method showed mobility as high as 0.1 cm^2/Vs. Other performance

parameters were extracted from the transfer characteristic curve and it showed I_{on}/I_{off} current ratio of 10^4, threshold voltage of -15 V, and subthreshold slop of 4.6 V/dec, respectively. In the single crystal structure, TIPSAN derivatives are slip-stack structure of core and end groups with short π-π stacking distance of 3.525 ~ 3.485 Å and large π-stacking area.

4. Summary

Newly designed TIPSAN derivatives exhibited mobility as high as 0.1 cm^2/Vs, I_{on}/I_{off} current ratio of 10^4, threshold voltage of -15 V, and subthreshold slop of 4.6 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.

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6. References

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