X-shaped Conjugated Organic Materials for High-mobility Thin Film Transistor

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Abstract

New X-shaped crystalline molecules have been synthesized through various coupling reactions and their electronic properties were investigated. They exhibit good solubility in common organic solvents and good self-film forming properties. They are intrinsically crystalline as they exhibit well-defined X-ray diffraction patterns from uniform and preferred orientations of molecules. They also exhibited high field effect mobilities in thin film transistor (TFT) and good device performances.

1. Introduction

Soluble organic semiconducting materials based on extended π-conjugated systems have received considerable attention for electronic devices over the last several years. Among various kinds of soluble organic semiconducting materials, star-shaped crystalline molecules have been highlighted to be synthesized because of their strong potential applications to organic field effect transistors (OFETs)[1-5] and organic photovoltaic devices.[6-8] Compared with linear organic conjugated oligomers and polymers used in OFETs, X-shaped molecules have a number of advantages including the ability to demonstrate multifunctionality in one molecule. The synthesis of π-conjugated star-shaped molecules raises the possibility of creating thiophene derivatives that are fully tethered to the aromatic core. Furthermore, the solubility problem in conjugated linear oligothiophene is totally overcome under a X-shaped architecture. Highly soluble, high mobility low molar mass molecules such as [1]benzotheno[3,2-b]benzothiophene derivatives, selenophene-containing heteroacene, silylethynylated polyacenes are not capable of achieving large-scale devices. Although some soluble semiconducting molecules were reported already, they all exhibited poor OTFT device performances. Herein we demonstrated high-performance OTFT fabrication based on solution process. The authors mention that this digest paper was written by using our previous reported results.[9,10]

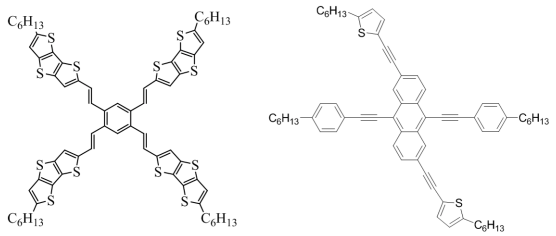
2. Experimental

The synthesis of the materials were already reported in the literature.[9,10] For the characterization of TFT performance, bottom gate top contact (or bottom contact) device geometry was employed. On the heavily n-doped Si/SiO_2 substrate the spin-coated films (thickness ~40-80 nm) were prepared with chloroform or monochlorobenzene as a solvent. Surface modification was carried out with bare silicon oxide or octyltrichlorosilane (OTS) to make hydrophobic dielectric surface. Source and drain electrodes were then thermally evaporated (100nm) through shadow mask with various channel width and length. All the field effect mobilities were extracted in the saturation regime using the relationship $\mu_{sat}=(2I_{DS}L)/(WC(V_g-V_{th})^2)$, where I_{DS} means saturation drain current, C is capacitance of SiO_2 dielectric, V_g is gate bias, and V_{th} is threshold voltage. The device performance was evaluated in air using Keithley 237 high voltage sourcemeter at ambient conditions.

3. Results and discussion

Two kinds of X-shaped conjugated large molcules are displayed in Figure 1. [1,2,4,5-tetra-(diethoxy-phosphorylmethyl)-benzyl]-phosphonic acid diethyl ester and thiophene-based carbaldehyde produces the conjugated-star-shaped molecule (a). The molecule (b) were synthesized with a yield of 75% by the Pd-

catalyzed Sonogashira coupling reaction of 2,6-dibromo-9,10-bis (phenylethynyl)anthracene and 2,6-dibromo-9,10-bis((4-hexylphenyl)ethynyl)anthracene with 2-ethynyl-5-hexyl thiophene.



(a) (b)

Figure 1. The structures of X-shaped conjugated molecules showing good FET mobilities. [9,10]

Two molecules were found to have good self-film forming properties and were well soluble in various organic solvents such as chloroform, xylene, MC, chlorobenzene, and THF. Compared to the decomposition temperature of dihexylsexithiophene (DH-6T), which is at around 309°C, these crystalline molecules have enhanced onset decomposition temperatures. Their thermal stabilities and dynamic behaviors are emphasized good for device fabrication

In order to study the crystallinity and preferred orientations of the X-shaped molecules, X-ray diffraction (XRD) was performed. The X-shaped molecular layers must be associated with the layered stacking properties brought about by the terminal alkyl groups, which are already known to induce long-range ordering. In the film samples, the preferred orientation is clearly inferred through the high reflection intensity of the peaks at a low angle((100) reflection) and the presence of peaks at a high angle ((010) reflection) region. They showed clear edge-to-edge transverse packing of the peripheral arms.

Because the moelcules possess very high solubility, thin-films were easily fabricated on a bare silicon oxide and an octyltrichlorosilane (OTS)-treated SiO_2 surface by simple spin-coating method using a >1.5 wt% monochlorobenzene (a) and chloroform (b) solution (2000-4000rpm, 30s). The source and drain electrodes were prepared onto the semiconductor surface via thermal evaporation. The mobilities were obtained from the source(S)-drain (D) current-voltage curves (I_{DS} vs V_{DS}) in well-resolved saturation regions. We obtain large field-effect mobilities of 0.03 cm^2/Vs (I_{on}/I_{off}= 1.0 x 10^3) and 0.24 cm^2/Vs (I_{on}/I_{off}= 5.4 x 10^6) for devices made of (a) and (b), respectively (see Figure 3 and Table 2). It should be noted that the mobilities larger than 0.1 cm^2/Vs have scarecely been achieved in devices of as-deposited film of organic semiconducting molecules.

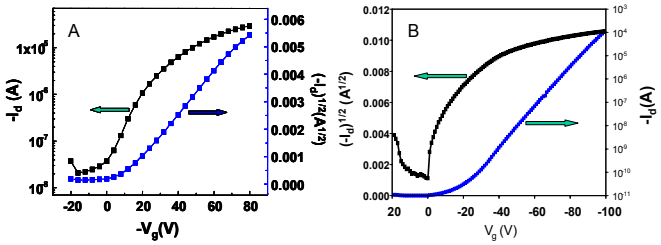


Figure 2. Plot of I_{DS} and $I_{DS}^{1/2}$ versus gate voltage (V_g) for OTFTs of (a) (A) and (b) (B).[9,10] ***The performances were measured at ambient conditions.**

4. Summary

In summary, we developed new X-shaped conjugated molecules for use as a highly soluble p-type organic semiconductor. The as-spun films were intrinsically highly crystalline and the molecules showed an edge-on orientation with regard to the substrate. The TFT device bearing the as-spun film of **2** showed greater enhancement of carrier mobility, which indicates that the uniform lamella and π-stacking of the 2-dimensional interactive molecule, facilitates the carrier transport phenomenon. Our study unambiguously demonstrates that the X-shaped molecules with a high degree of molecular arrangement, and high solubility can be fully utilized for fabricating improved OTFT devices.

Acknowledgement

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5. References

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