

Development of High-Performance Organic Field-Effect Transistors via Surface-Mediated Molecular Ordering

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Abstract

We report on high-performance organic field-effect transistors by promoting surface-mediated two-dimensional molecular ordering in organic semiconductor. To achieve this goal, we have controlled the intermolecular interaction at the interface between organic semiconductor and the insulator substrate.

1 Objectives and Background

Regioregular P3HT has recently been incorporated as the active material in field-effect transistors (FET) in which a preferential supramolecular two-dimensional ordering of the polymer chains with high regioregularity induces a high field-effect mobility of up to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, approaching that of single crystal oligothiophenes.¹ Among the factors affecting field-effect mobility, the molecular ordering of nanocrystallites in thin films of regioregular P3HT has been the most extensively investigated²⁻⁴. In order to enhance two-dimensional molecular ordering, many groups have examined the outcomes of modifying the molecular parameters (regioregularity, molecular weight and side-chain length) and processing conditions (solvent power, film thickness, doping level and film forming method). Despite the resulting improvements in the field-effect mobility of regioregular P3HT, little is yet known about how the interface between regioregular P3HT and the insulator is stabilized and how the orientations of P3HT chains at the interface can be optimized to obtain higher mobilities. Herein, we focus on controlling the structural ordering that results from the intermolecular interactions at the interface between regioregular P3HT and the insulator (SiO_2) with the aim of enhancing the two-dimensional molecular ordering of thin films of regioregular P3HT. We show in this paper that

there is a clear correlation between the field-effect mobility of regioregular P3HT and the surface-mediated orientation (parallel and perpendicular) of P3HT chains with respect to the insulator substrate.

2 Results

We used a simple spin-casting method to fabricate regioregular P3HT thin films with a thickness of about 70–80 nm. The resulting thin films were annealed at 240 (above the melting temperature of P3HT) for 20 minutes and cooled down to room temperature in order to increase the regularity of the backbone conformation. Surprisingly, two different chain orientations (edge-on orientation and face-on orientation) of the nanocrystalline regioregular P3HT domains with respect to the insulator substrates modified by SAMs were identified. The two different orientations are evident from the different intensity distributions of the (100) reflections due to the lamellar layer structure (16.4 Å) and the (010) reflections due to π - π interchain stacking (3.8 Å) through out-of-plane and in-plane geometric mode. The degree of orientational anisotropy was found to depend strongly upon the surface characteristics of the insulator substrate. In samples (P3HT_ NH_2 and P3HT_ OH) on insulator substrates with unshared electron pairs ($-\text{NH}_2$ and $-\text{OH}$) the preferential orientation of the ordered domains was found to be along the (100)-axis normal to the P3HT film and the (010)-axis in the plane of the film. Particularly, the P3HT_ NH_2 film has a more perfectly perpendicular orientation with respect to the insulator substrate than found in the P3HT_ OH film. In contrast, most of the crystallites in samples (P3HT_ CH_3) on insulator substrates without unshared electron pairs ($-\text{CH}_3$)

are preferentially oriented along the (100)-axis in the plane and the (010)-axis normal to the P3HT film.

This anisotropy in molecular ordering is clearly an important influence on the field-effect mobility of P3HT thin film transistors, since this perpendicular orientation ensures that delocalized intermolecular states are formed in the direction parallel to the insulator substrate, which is the transport direction in the field-effect transistor. This ability to control the chain orientation and crystalline order allows us to establish a direct correlation between the direction of π - π stacking and the in-plane field-effect mobility.

In order to determine the relationship between molecular ordering and field-effect mobility, the field-effect mobilities of regioregular P3HT were measured using a bottom-contact thin-film field-effect transistor (FET) geometry. It shows that the annealing process results in field-effect mobilities (0.08 – $0.28 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) that are higher by more than a factor of $8 \sim 30$ than those of the as-prepared samples ($0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). For samples annealed under the same conditions, the highest mobilities are observed for the P3HT-NH₂ sample ($0.28 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

This surprising increase in the field-effect mobility is attributed to the perpendicular orientation with respect to the insulator substrate (in the P3HT-NH₂ case).

3. Impact

We conclude that surface-mediated molecular ordering has a substantial effect on the preferential orientations of the P3HT chains, and that this effect can be used to enhance the field-effect mobility. In order to enhance the field-effect mobility by making use of surface-mediated two-dimensional molecular ordering in regioregular P3HT, we controlled the intermolecular interactions at the interface between P3HT and the insulator substrate by using various functionalized self-assembled monolayers (-NH₂ and -CH₃), SAMs, and compared the results obtained for these systems with those for the bare insulator substrate, which has -OH group functionalization. We found that, depending on the surface properties, the P3HT nanocrystals can adopt two different orientations – parallel and perpendicular to the

insulator substrate – the field-effect mobilities of which differ by more than a factor of 4, and which can reach the values as high as $0.28 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

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