Surface-Induced Self-Assembly of Conjugated Organic Molecules for High-Performance Organic Thin Film Transistors

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Control over surface induced self-assembly of electronically active pi-conjugated molecules provides great opportunities to fine-tune and optimize their electrical properties for applications in organic electronics [1-3]. The design of substrates with controllable surface properties can be effectively achieved employing functionalized self-assembled monolayers (SAMs), which have become one of the most popular techniques to create well-defined functional nanostructures [4-6]. By self-assembly of pi-conjugated nanostructures with strongly pi–pi interacting building blocks via surface chemistry [7-8], even the highest mobilities and possibly, a truly delocalized transport regime, may be attained.

In this study, with the aim of enhancing the electrical performances by promoting surface induced two-dimensional self-assembly in representative pi-conjugated molecules such as poly (3-hexylthiophene) (P3HT) and pentacene, we have controlled the intermolecular interaction at the interface between pi-conjugated molecules and substrate by using self-assembled monolayers (SAMs) functionalized with various groups. We will discuss the dependency of pi-conjugated molecules on the specific properties of the substrate surface and the effect of surface induced self-assembly on electrical performances in organic transistors.

In the first system, we explicated the preparation and properties of high-performance polymer transistors via surface-induced molecular ordering, which offers a promising protocol for the bottom-up assembly of new flexible electronics. To achieve this goal, we used a simple spin-casting method to fabricate regioregular poly (3-hexylthiophene), P3HT thin films with a thickness of about 70–80 nm on insulator substrates having various surface chemistry [3,9-10]. 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 (Fig. 1). 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 [1].

In samples (P3HT_NH₂ and P3HT_OH) on insulator substrates with unshared electron pairs (-NH₂ and -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_NH₂ 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_CH₃) on insulator substrates without unshared electron pairs (-CH₃) 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 the bottom-contact thin film field effect transistor (FET) geometry. The field-effect mobility is changed with annealing and with surface characteristics. It shows that the annealing process results in field-effect mobilities (0.08–0.28 cm²V⁻¹s⁻¹) that are higher by more than a factor of 8 ~ 30 than those of

the as-prepared samples (0.01 cm²V⁻¹s⁻¹). For samples annealed under the same conditions, the highest mobilities are observed for the P3HT_NH₂ sample (0.28 cm²V⁻¹s⁻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).
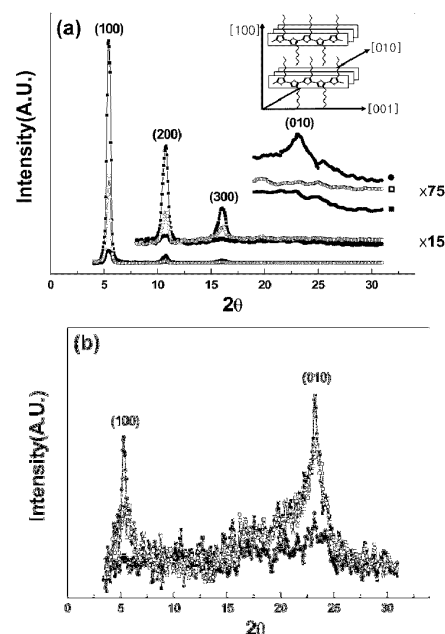

Figure 1. Out-of-plane (a) and in-plane (b) grazing incidence angle X-ray diffraction intensities as a function of the scattering angle 2θ for regioregular P3HT thin films crystallized against insulator substrates modified with different SAMs. The insets show schematically the crystallography of the nano-crystallite with respect to insulator substrate. ■ P3HT_NH₂, □ P3HT_OH, ● P3HT_CH₃.

In the second system, we could control the crystalline microstructures such as crystalline phase and grain size by changing the physical states (molecular structures) of organosilane SAMs treated on silicon dioxide gate dielectrics [11-12]. We found that, depending on the physical states of dielectric surfaces, the pentacene nanocrystals can adopt two different crystalline phase near the interface – kinetically favored "thin-film phase" and thermo-dynamically stable "bulk phase", affecting the grain size of pentacene thin film – the field-effect mobilities of which differ by more than a factor of 3, and which can reach the values as high as 0.6 cm²V⁻¹s⁻¹ [13]. This surprising increase in the field-effect mobility is due to the large gains with thin-film phase in the pentacene films. Also, this phenomenon can be explained by the following factor: less ordered state of organosilane SAMs (OTS case) with short alkyl chains results in somewhat promoted mobility of the pentacene molecules on the dielectric surface, which contributes to the production of the kinetically favored phase (thin-film phase) and large grains in pentacene thin films.
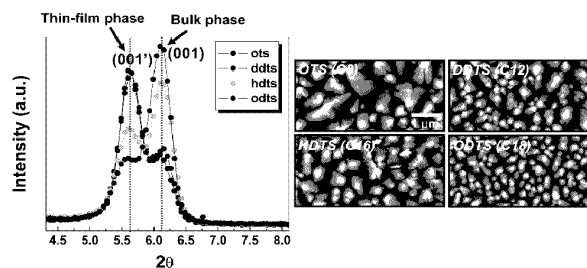

Figure 2. Typical 1-D grazing incidence X-ray diffraction profiles in the direction of out-of-plane and TM-SFM topography images of 60 nm-thick pentacene films deposited on OTS-, DDTS-, HDTS-, and ODTS-treated gate dielectrics.

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