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Organic Thin-Film Transistors Based on α,ω-Dihexyldithienyl-Dihydrophenanthrene

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There is considerable interest in low-cost organic alternatives such as higher oligoacenes and oligothiophenes to amorphous silicon for integration into thin-film transistor (TFT) devices.[1−3] Organic materials may provide advantages over conventional inorganic materials, including facile processability and compatibility with flexible substrates[4−6] and organic TFTs can display field effect mobility (μ_{fe}) values as high as 3.0 cm^2/(V s).[7] Such characteristics have prompted research for alternative core structures and the introduction of new functionalities.[8−10] Incorporation of alkyl chains onto the periphery of the delocalized core is important to improve intramolecular $\pi-\pi$ stacking and the microstructure at the semiconductor/dielectric interface.[4,11,12] Garnier et al. found that μ_{fe} increases by a factor of 25 upon introduction of hexyl substituents at the α- and ω-positions of sexithiophene.[11] Oikawa et al. and Bao et al. also reported heteroarene structures bearing alkyl chains that have a high carrier mobility because of highly ordered smectic mesophases.[13] According to these studies, highly ordered thin films with strongly interacting polycrystalline grains are necessary to achieve high μ_{fe} values. Herein, we report the facile synthesis of a new organic semiconductor, 2,7-bis-(5′-hexyl-2,2′-bithien-5-yl)-9,10-dihydro-phenanthrene (**HT-PT**) (see Scheme 1), and its use in the fabrication of organic TFTs. Of significance is that TFT devices with **HT-PT** as the semiconducting layer exhibit hole mobilities in the range of 0.42 cm^2/(V s).

HT-PT was synthesized from the corresponding 2,7-diiodo-9,10-dihydrophenanthrene (**1**) and 5′-hexyl-2,2′-bithiophene-5-boronic ester (**2**) using the palladium-catalyzed

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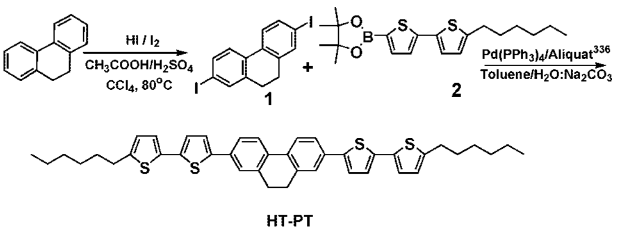
Scheme 1. Synthetic Route for HT-PT



Suzuki cross-coupling reaction[14,15] and was isolated as a greenish yellow solid. It is a thermally stable solid that is readily purified by recrystallization.

X-ray diffraction (XRD) analyses were performed on **HT-PT** films vacuum-deposited onto Si/SiO$_2$ substrates. The thin films were deposited on Si/SiO$_2$ substrates as a 30 nm thickness. The results of these studies are shown in Figure 1. A comparison was made as a function of whether the dielectric surface was treated with octyltrichlorosilane (OTS) and of thermal treatment, which involved heating to 160 °C for 10 min. The thermal properties of the **HT-PT** were measured by differential scanning calorimetry (DSC), and the curves from the third heating/cooling cycle are shown in below. The first crystalline temperature is at 157 °C. The annealing temperature was chosen to correspond to the first crystalline temperature observed by DSC analysis. These data were deposited as Supporting Information.

Figure 1a shows that the intensity of the first peak (001) in the XRD patterns of films deposited atop untreated SiO$_2$ increases slightly after annealing at 160 °C. These observations are consistent with an increase of the film crystallinity. Films deposited on OTS-treated surfaces were found to be more crystalline than films deposited atop untreated Si/SiO$_2$. When both annealing and OTS treatment were performed, the XRD patterns show sharp reflections up to the second order and are consistent with a high degree of crystallinity,[16,17] as illustrated in Figure 1b. Additionally, the molecular alignment on the dielectric surface can be estimated by comparing the calculated molecular length to the length derived from the *d*-spacing distance. From the MM2-minimized molecular length obtained by using CS Chem3D and the *d*-spacing distance obtained from the XRD results, we estimate the actual molecular distance to be 37.4 Å and the thickness of the single film layer to be 31.8 Å. The (001) reflection at 31.8 Å is approximately correlated with the length of a molecule. That these two distances are similar implies the presence of perpendicular stacking relative to the dielectric surface and a well-aligned $\pi-\pi$ intermolecular structure.

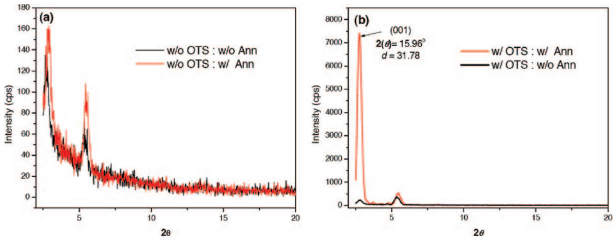


Figure 1. X-ray diffraction patterns for vacuum evaporated films of **HT-PT**. (a) No OTS-treated/no annealed film (black) and no OTS- treated/annealed film (red), (b) OTS-treated/no annealed film (black) and OTS-treated/annealed film (red).

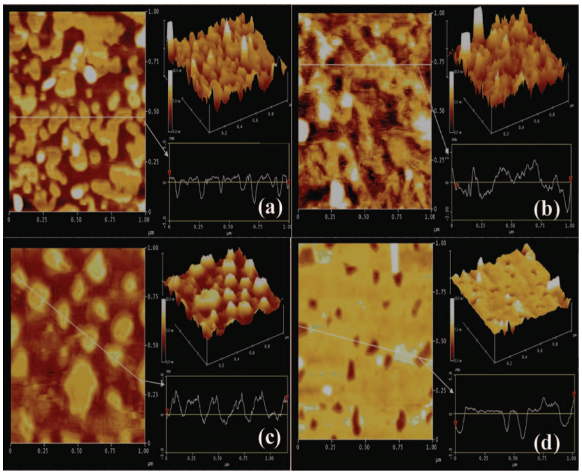


Figure 2. AFM images (1 μm × 1 μm) of the HT-PT layers as a function of treatment: (a) without-OTS/without-annealing, (b) without-OTS/with-annealing, (c) with-OTS/without-annealing, and (d) with-OTS/with-annealing.

Table 1. Performance Parameters of HT-PT **TFT Devices**

	bare SiO$_2$		OTS-treated SiO$_2$	
	without-Ann	with-Ann[a]	without-Ann	with-Ann[a]
mobility (cm^2/Vs)[b]	0.02	0.04	0.13	0.42
on/off ratio[b]	1×10^5	1×10^6	1×10^5	1×10^6

[a] After annealing at 160 °C, the devices were cooled slowly. [b] All devices were measured under N$_2$.

Atomic force microscopy (AFM) examination of surface properties shows that the thin-film morphologies consist of uniformly arranged grains in Figure 2. Larger grain sizes and a more homogeneous surface uniformity are obtained when both OTS treatment and annealing are carried out. It appears that OTS treatment of SiO$_2$ weakens substrate−molecule repulsion. Furthermore, the presence of the hexyl group side chains strengthens lateral interlayer interactions. These conditions lead to the formation of interconnecting grains, which are anticipated to improve the charge carrier mobility. From these XRD and AFM results, we conclude that thermal treatment increases the crystallinity of the film by strengthening the intermolecular interactions between heteroarene units, and OTS treatment is helpful to align the molecules perpendicular to the surface.

TFT devices were fabricated with a top contact geometry using Au electrodes as described in the Supporting Information. The channel width and length were 1500 and 50 μm, respectively. The μ_{fe} values were obtained using the source-drain current (I_{ds}) in well-resolved saturation regions, please refer to Table 1 for a summary of results. Accordingly, we obtained the following characteristics for the OTS-treated/thermally annealed device: $\mu_{fe} = 0.42$ cm^2/(V s) and an on/off ratio of 1×10^6, with output characteristic curves that

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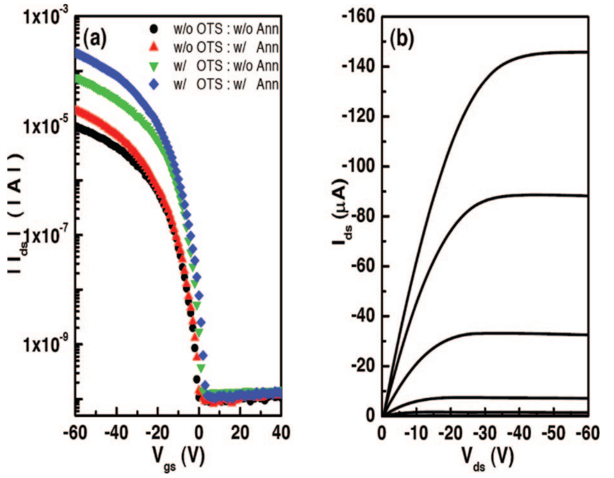

Figure 3. (a) Transfer characteristics of TFT devices with HT-PT as the organic semiconducting layer; (b) output characteristics of the devices with OTS-treated surfaces and thermal annealing.

exhibit so-called "perfect" saturation as shown in Figure 3. In addition, the hole mobility and on/off ratio of the non-OTS treated/nonannealed device were $\mu_{fe} = 0.02$ cm^2/(V s) and $I_{on}/I_{off} = \sim 1 \times 10^5$, respectively. Thus, μ_{fe} can be increased by approximately a factor of 20 by proper management of the dielectric surface characteristics and by providing sufficient thermal energy for the system to optimize π-π packing among molecular units. It is also noteworthy that the performance of **HT-PT** is higher by a factor of 10 when compared against structurally related phenanthrene derivatives reported previously.[18] We suggest that the reason for this improvement is due to the lower melting crystalline temperature of **HT-PT**, which was anticipated on the basis of the melting temperatures of the two internal cores.[19]

In conclusion, we have designed a novel thiophene−phenanthrene-based semiconducting material, **HT-PT**, which is straightforward to synthesize, as shown in Scheme 1. Structural characterization shows that **HT-PT** forms a highly ordered polycrystalline film, which we attribute to its (1) good intermolecular packing properties, (2) good alignment of the molecules to the device surface, and (3) excellent molecular planarity. Preparation and characterization of organic TFTs with **HT-PT** semiconducting layers show that the OTS treatment of the dielectric, in combination with thermal annealing near the crystalline temperature can give rise to performance parameters that include a high hole mobility ($\mu_{fe} = 0.42$ cm^2/(V s)) and a high on/off ratio ($I_{on}/I_{off} = \sim 1 \times 10^6$). There is the potential for further improvement by carrying out more rigorous purification/isolation protocols and by adjusting device fabrication procedures. From a broader perspective, this work illustrates how seemingly minor changes in the constitution of the molecular components, i.e., "hydrogenation" of phenanthrene to give the 9,10-dihydrophenanthrene core, yields drastic changes in the electronic properties of the bulk material.[20] Our current thinking is that the improved performance stems from the differences in thermal properties, which influence organization as a function of processing history and can be traced back to the thermal behavior of the core constituents.

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Supporting Information Available: Detailed synthesis procedures for HT-PT, UV−vis spectroscopy, additional TFT data, and DSC analysis (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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