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α,*ω*-Dihexylquaterthiophene: A Second Thin Film Single-Crystal Organic Semiconductor

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The crucial component in complex all-printed or all-organic electronic circuits is projected to be the organic-based thin film transistor (TFT), in which a polymeric or molecular solid acts as the semiconductor.[1] This semiconductor must support a "channel" of holes or electrons that is induced by a "gate" voltage that turns the device "on", and the mobility of charges in the channel must be sufficient to increase the on-conduction between "source" and "drain" electrodes by many orders of magnitude over the "off" state. A variety of parent chemical structures have been considered for the semiconducting compound, including polyacenes;[2] oligothiophenes;[3] polythiophenes,[4] -thienylenevinylenes,[5] and -pyrroles;[6] phthalocyanines;[7] carbon−sulfur fused rings;[8] electron-deficient naphthalenes;[9] and fullerene.[10] Mobilities range from immeasurably low (below 10^{-6} cm^2/Vs) to the 0.1−1 cm^2/Vs range comparable to the mobility of amorphous silicon. The largest mobility observed so far in an organic TFT has been that of pentacene, which can be engineered to a mobility greater than 1 cm^2/Vs.[11] This extraordinary mobility has been attributed to the unique single-crystalline ordering[12] and continuity that can be obtained when pentacene is deposited under particular conditions. The organization and continuity of this type of pentacene film are probably responsible for at least an order of magnitude enhancement in the mobility.

Our investigation of thiophene oligomers as TFT semiconductors has evolved to emphasize compounds with greater solubility and potential liquid-phase processibility than the prototypical α-sexithiophene (α6T). We have therefore developed synthetic methods[13] aimed at oligothiophenes with shorter conjugated cores and solubilizing end-substituents and have screened several such compounds for their semiconducting properties, including the title compound, α,*ω*-dihexylquaterthiophene (DHα4T), which has also been investigated elsewhere.[14] This communication reports the striking observation of exceptional single-crystal ordering in sublimed films of this compound and, as was observed in pentacene, a

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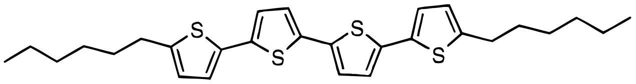

DHα4T

correspondingly dramatic increase in the mobility compared to non-single-crystalline α4T analogues.

DHα4T was synthesized using an embodiment of our "polar intermediate" strategy for preparing thiophene oligomers of the highest purity, first acylating bithiophene with hexanoic anhydride, reducing the isolated monoketone, and dimerizing the resulting 5-hexyl-2,2′-bithiophene with BuLi/$CuCl_2$ as usual. The details are provided in the accompanying full paper[15] that also covers a series of related α4T and α6T derivatives. The compound was purified by sublimation (NMR 0.87, 1.3, 1.7, 2.75 (side chain CH), 6.68, 6.9−7.0 (ArH); CHS within 0.2 of theoretical percentages) and vacuum deposited at ca. 10^{-6} Torr simultaneously onto SiO_2-covered silicon substrates, as well as carbon grids, held at temperatures ranging from ambient to 100 °C. For TFTs, the underlying silicon was heavily n-doped to serve as a gate electrode. Gold source and drain electrodes were deposited on top of the DHα4T films to complete the TFT fabrication, the so-called "top-contact" TFT geometry.

Transmission electron microscopy of the films on carbon grids reveals a very smooth and flat morphology of lamellar single crystals (see Figure 1). In Figure 1a, the typical morphology at low deposition temperatures (e.g., 50 °C) is seen to consist of multilayers of such lamellae extending to micrometers in lateral dimensions. From controlled oblique shadowing with Pt, we estimated the lamellar thickness at ca. 15 nm, which means that the crystals consist of 5−6 molecular layers. At high deposition temperatures (e.g., 100 °C, Figure 1b) the flat crystals now extend over many tens of micrometers and no longer exhibit substantial multilayering. Their only distinguishing feature is the existence of transverse cracks (similar to those that we have reported earlier for α6T.[16] Because these are not seen for DHα4T films deposited at lower temperatures, they are most likely the result of contraction during cooling.

Electron diffraction yields sharp spotty patterns even with room temperature deposition. These become progressively more single-crystal-like at higher deposition temperatures. Above 50 °C the patterns are essentially single crystalline from areas covering tens of micrometers in diameter (see Figure 2). At 100 °C deposition, the diffraction pattern normal to the surface reveals a rectangular lattice with axes of 7.84 and 5.96 Å.

X-ray diffraction of the films grown on Si/SiO_2 shows a series of sharp peaks, all corresponding to successive orders of the molecular repeat at 28.5 Å (see Figure 3). The sharpness of the peaks increases, as expected, with deposition temperature. The 28.5 Å molecular repeat is consistent with molecules being essentially normal to the substrate and with their hexyl chains directed toward the sulfur side of the 5 and 5‴ positions of the quaterthiophene core.

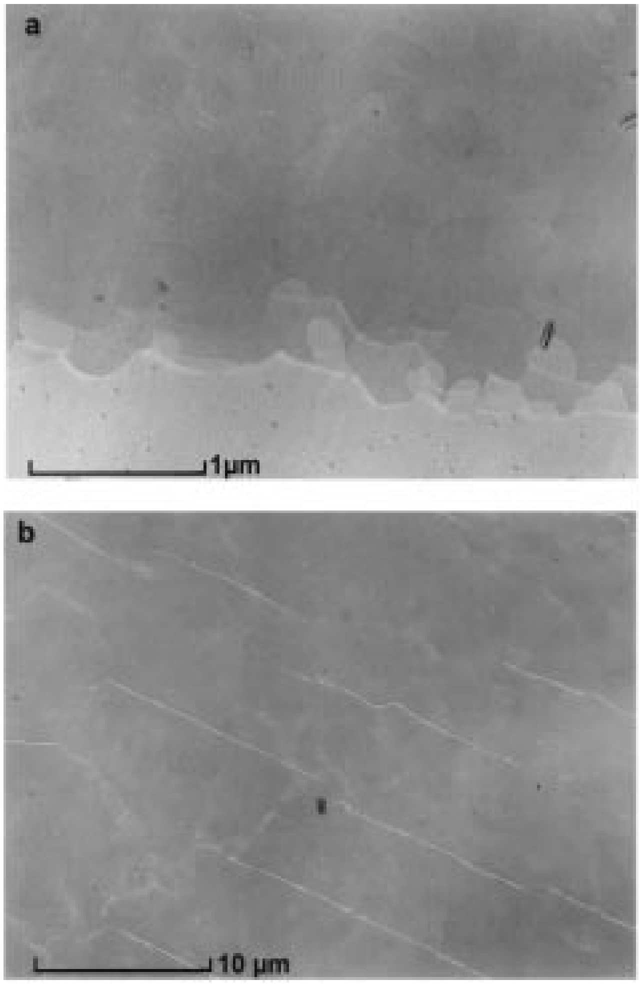

Figure 1. Transmission electron micrographs of DHα4T films deposited at T_{sub} = (a) 50 °C and (b) 100 °C.

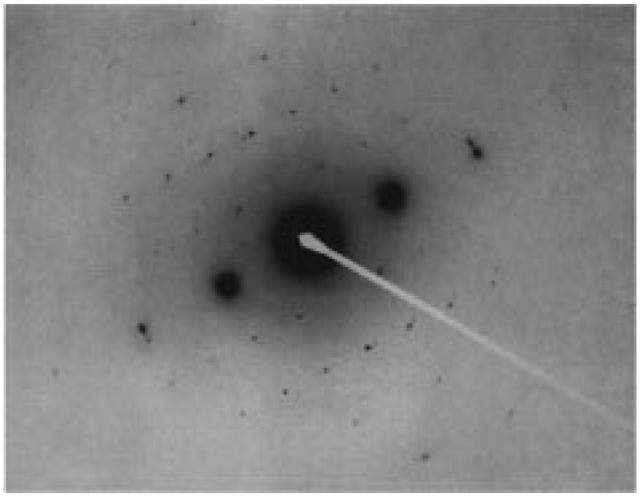

Figure 2. Selected-area diffraction pattern of a DHα4T film deposited at T_{sub} = 100 °C.

TFT mobilities of these films are listed in Table 1 for a channel width (*W*) to length (*L*) ratio of ca. 1.5. The channel current increases as the gate voltage is made more negative, indicating that the primary charge carriers are holes and that the device operates in the enhancement mode. The areas of the devices are ca. 4 × 10^{-2} mm^2. An order of magnitude drop in the apparent mobility was observed for larger devices deposited at room temperature, with *W*/*L* of 4 and areas

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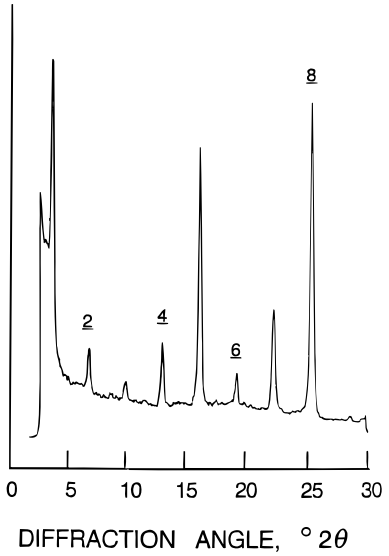

Figure 3. X-ray diffractogram of DHα4T films deposited on Si/SiO$_2$ by sublimation at T_{sub} = room temperature.

Table 1. Field-Effect Mobilites of DHα4T at Different Substrate Deposition Temperatures and Channel Dimensions

	mobility, cm^2/Vs	
temp, °C	*W*/*L* ca. 1.5/1	*W*/*L* = 4/1
RT[a]	0.16 ± 0.013	9×10^{-3} ± 0.001
50	0.12 ± 0.01	0.06 ± 0.01
80	0.23 ± 0.02	
100	0.046 ± 0.003	0.039 ± 0.01

[a] RT = room temperature.

of ca. 4 mm^2, and may be caused by the greater likelihood of encountering a catastrophic defect or trap in a much larger active area. The lower observed mobility of the 100 °C devices compared to the others may be a result of the formation of long cracks (tens of micrometers according to Figure 1b) during cooling, which could arise from the mismatch in coefficient of thermal expansion between the substrate and the DHα4T active layer. The 80 °C mobility is higher than has ever been observed in a thiophene *hexamer*, as high as has ever been observed in any *polycrystalline* organic semiconductor, and is over an order of magnitude higher than the highest reported mobility of the parent α4T. As was the case in pentacene, we believe the high mobility is correlated with the single-crystal nature of the organic semiconductor film.

It is remarkable that of the many organic compounds screened so far for semiconducting activity, especially p-channel activity, only pentacene and DHα4T have been shown to form large-area single-crystal films. Their structures represent extremes in the group in that pentacene is an all-hydrocarbon, high-melting, unsubstituted fused ring while DHα4T is a much lower melting, substituted, thiophene-based compound. While the molecular design rules for high mobility on a molecular scale appear to be coverging on a need for rigidity, planarity, and specific oxidation/reduction potentials[17] or orbital energies, the molecular features that lead to single-crystal-like ordering with perpendicular orientation, ideal for TFTs, remain undefined. The attainment of this preferred morphology using liquid-phase deposition methods instead of high-vacuum sublimation is a critical and challenging goal of our current research.

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