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Communication

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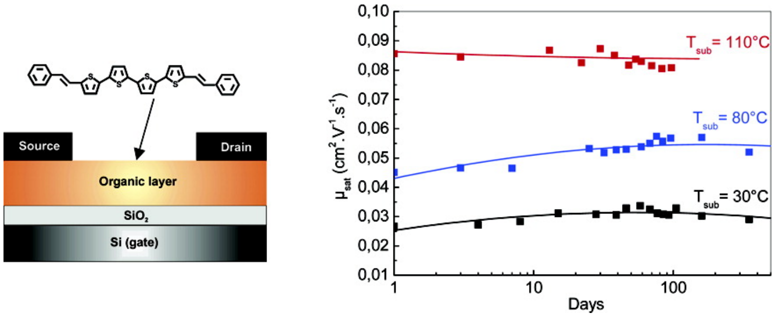

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α,ω-Distyryl Oligothiophenes: High Mobility Semiconductors for Environmentally Stable Organic Thin Film Transistors

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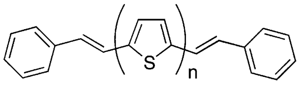
The urgent needs in novel information technologies are giving considerable impetus to the field of organic electronics.[1] Clearly, organic semiconducting materials offer themselves as unique alternatives to amorphous silicon in low-cost applications, where easy processability is desirable, such as the fabrication of large area, flexible devices, and circuits via liquid deposition techniques.[2] Organic thin film transistors (OTFTs) are essential for the development of organic electronic devices.[1,2a] High-performance electron- or hole-transporting materials that display both high charge carrier mobilities and processing versatility have been reported.[3−5] Critical to the exploitation of OTFTs in commercial applications is the improvement of the device's environmental stability. Very recently, several groups reported significant enhancements of OTFTs' stability under ambient conditions in the case of semiconducting small molecules,[4] oligomers,[5,6] and polymers.[7] Exceptional stability features were described for acene−thiophene semiconductors.[5]

The oligothiophene skeleton is among the most versatile and effective molecular scaffold on which to base the rational design of organic semiconductors.[8] However, oligothiophene derivatives are generally recognized to offer only poor air stability, and the fact is that their OTFTs show rapid performance degradation.

In this communication, we report a new series of structurally simple and readily available oligothiophenes end-capped with styryl units, **DS-*n*T** ($n = 2{-}4$), that were used as the semiconducting layer in OTFTs (Scheme 1).[9] The devices not only show very high field-effect mobility (up to 0.1 cm^2/Vs) and on/off ratios (up to 10^5) but also are found to be exceptionally long-lived (more than 1 year of storage) and stable toward continuous operation, under atmospheric conditions. To our knowledge, compound **DS-4T** is the first example of a long-chain oligothiophene derivative that allows one to fabricate highly stable OTFTs with a life of more than 17 months. High mobility is usually obtained for long thiophene oligomers, but this usually is at the expense of the device's stability owing to the lower oxidation potential of such structures. Remarkably, this is not the case with **DS-4T**, as this compound, containing the tetrathiophene core, indeed shows the highest stability along with the best electrical characteristics within the series investigated.

Styryl end-substitution was selected because (i) the introduction of double bonds in oligothiophenes was shown to produce planar structures with reduced overall aromatic character,[10] (ii) thiophene backbones containing phenylene units were observed to give rise to efficient OTFTs,[11] and (iii) the benzene moieties represent versatile termini for further incorporation of solubilizing or self-assembling groups.[12] Compounds **DS-*n*T** were synthesized[13] according to Scheme S1 and were characterized by ^{1}H NMR, mass spectrometry, and elemental analysis.

Scheme 1



DS-nT
n = 2, 3, 4

UV−vis/fluorescence data point to a more extended electron conjugation pathway within the distyryl derivatives, as indicated by the substantial red-shift in absorption and emission maxima ($\lambda_{abs}/\lambda_{em}$ (nm): **DS-2T** 425/477; **DS-3T** 445/506; **DS-4T** 455/524) relative to the parent oligothiophenes, such as **4T** ($\lambda_{abs}/\lambda_{em} = 393/451$ nm). Accordingly, optical gap values were found to be reduced (E_g (eV): **DS-2T** 2.6; **DS-3T** 2.45; **DS-4T** 2.37; **4T** 2.8). Cyclic voltammetry measurements of **DS-*n*T** show a set of separate reversible one-electron oxidations ($E_{1/2}(1)/E_{1/2}(2)$ (V): **DS-2T** 1.03; **DS-3T** 0.95/1.17; **DS-4T** 0.85/1.08). The first oxidation of **DS-4T** occurs at a considerably less positive potential than that recorded for **4T** ($E_{1/2}(1) = 1.18$ V).

OTFT devices were fabricated using the top contact geometry (Figure S1). Each entry in Tables 1 and S1 lists the OTFT data as a range obtained in air for 10 independent devices. Transistor responses were obtained only for positive bias, which is indicative that **DS-*n*T** compounds are p-type semiconductors (Figure 1, left). The field effect mobilities calculated in the saturation regime are shown to increase with the substrate deposition temperature, due to the formation of better ordered thin films at elevated T_{sub}. The highest value of the hole mobility (0.1 cm^2/Vs) was obtained for the longest oligomer (**DS-4T**) at 110 °C. Increasing the substrate temperature to 140 °C led to a decrease of the device performance, as observed for other organic semiconductors.[5] The mobility and on/off ratios of OTFTs based on a silicon oxide insulator layer coated with hexamethyldisilazane (HDMS) were not significantly improved relative to the unmodified samples (Table S2). However HDMS treatment was observed to decrease the threshold voltages, V_t, and also their range of variation.[14]

The morphology of vapor-deposited thin films of **DS-4T** grown on SiO$_2$/Si was investigated using AFM. Picture in Figure 1 (right) shows the formation of islands whose size increases with the substrate deposition temperature. At $T_{sub} = 110$ °C, a terrace-and-step morphology is clearly observed, an average value of 2.9 nm being determined for the step height. A **DS-4T** thin film deposited on SiO$_2$/Si at room temperature was investigated by X-ray diffraction in the reflection mode. Sharp and strong reflections up to the 9th order confirm the high degree of lamellar ordering even at low deposition temperature (Figure S2). The *d*-spacing obtained from the peak at $2\theta = 3.15°$ is 2.802 nm, which is in agreement with the AFM results.

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Table 1. OTFT Data of the Semiconductors **DS-*n*T** Deposited at Different Substrate Temperatures on Silicon Oxide Layers

material	T_{sub} (°C)	μ (cm^2/Vs)	on/off	V_t (V)
DS-2T	30	0.002−0.006	$1.6−1.9 \times 10^5$	4−8
	80	0.01−0.02	$2−2.3 \times 10^5$	0−19
DS-3T	30	0.001−0.008	$2.2−2.8 \times 10^4$	0.1−3
	80	0.01−0.02	$2.2−3.3 \times 10^4$	4−13
DS-4T	30	0.02−0.04	$1.2−1.8 \times 10^3$	3−13
	80	0.03−0.06	$1.9−2.5 \times 10^3$	12−20
	110	0.08−0.1	$0.8−1.2 \times 10^3$	5−20
	140	0.05−0.07	$1.5−2 \times 10^3$	9−22

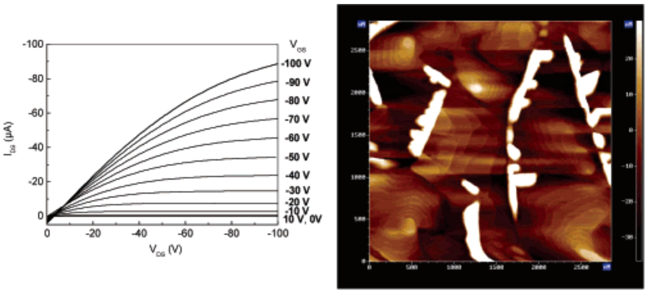

Figure 1. (Left) Plot of I_{DS} versus V_{DS} at various gate voltages in a **DS-4T**-based OTFT device fabricated at $T_{sub} = 110$ °C. (Right) AFM picture (scale = 2.8 μm × 2.8 μm) of a **DS-4T** thin film evaporated on SiO$_2$/Si at $T_{sub} = 110$ °C.

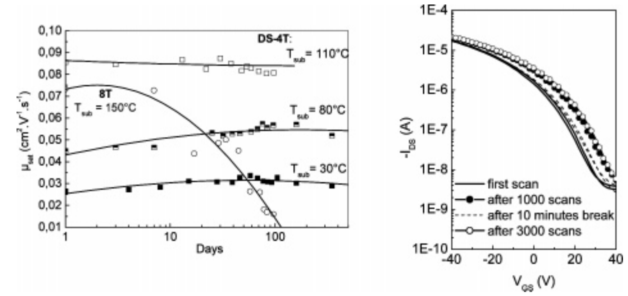

Figure 2. Characteristics of **DS-4T** OTFT devices on SiO$_2$/Si. (Left) Plots of hole mobilities (μ) versus storage days for OTFTs fabricated at different substrate deposition temperatures (T_{sub}). (Right) Plots of I_{DS} versus V_{GS} at constant $V_{DS} = -40$ V at $T_{sub} = 80$ °C after 17 months of storage.

OTFT devices were stored over 17 months in the dark under ambient conditions, and device performances were measured periodically. Figure 2 (left) illustrates the stability of the hole mobility values obtained for **DS-4T** films deposited at three temperatures onto unmodified SiO$_2$/Si substrates. In contrast, the mobility value determined under the same conditions for the octithiophene semiconductor (**8T**, $T_{sub} = 150$ °C) showed a decrease of about 70% of its initial value (0.073 cm^2/Vs) after 100 days. In the case of the shorter derivatives, **DS-2T** and **DS-3T**, the mobility values remained constant over 100 days, but a decrease of about 20−50% of the initial device performance appeared on a shelf-life time test of 10 months. Strikingly, the highest device stability was obtained for **DS-4T**, the compound with the highest HOMO energy level within the **DS-*n*T** series, which is in contrast with previous observations.[6] Although this behavior still remains unclear, an increase of doping level over time for the more oxidizable **DS-4T** oligomer can be ruled out at this stage as no change, and especially no decrease, of the on/off ratio was noticed upon storage. Moreover, the V_t value determined for each independent device did not show significant change over time.

A **DS-4T** OTFT device that had been stored over 17 months has been subjected to a continuous sweeping of gate−source voltages (-40 V $< V_{GS} < +40$ V) under a constant drain−source voltage ($V_{DS} = -40$ V) (Figure 2, right). After a first series of 1000 double scans, a small increase of I_{DS} was observed, which almost overlapped the initial value after a rest period of 10 min. Then a series of 3000 double scans was further applied, which led to a similar shift-recovery for I_{DS} and to no degradation of performances (μ, V_t, and on/off ratio). These results show that the 17 months old devices are stable under continuous operation conditions. A possible reason for the reversible shift observed for I_{DS} in these experiments could be an increase of the device temperature during operation or a reversible charging effect at the semiconductor−dielectric interface.

In conclusion, distyryl oligothiophenes represent a novel class of OTFT semiconductors that combine good electrical performances and exceptional stabilities. The synthesis of soluble and n-type analogous derivatives is currently underway for applications in flexible electronics.

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Supporting Information Available: **DS-*n*T** syntheses, details of experimental procedures in solution, OTFT device fabrication, X-ray diffraction procedure; Scheme S1; Figures S1, S2; Tables S1, S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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