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Solution Processable Organic Field-Effect Transistors Utilizing an α,α′-Dihexylpentathiophene-Based Swivel Cruciform

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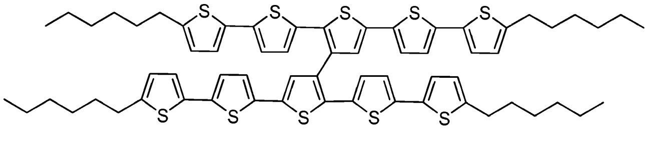
Research into the application of organic field-effect transistors (OFETs) has intensified of late, and the progress has been considerable.[1] One of the most attractive features of such OFETs is the possibility to use liquid-phase techniques such as ink-jet printing or spin coating.[1f,2] This aspect is deemed crucial if the transistors are to be implemented on large, flexible substrates in a cost-effective manner. Two primary synthetic modus operandi have emerged toward achieving the desired properties of solubility and favorable packing in organic thin films, namely via the polymeric and small-molecule approaches. Semiconducting polymers such as poly(3-hexylthiophene) exhibit good film-forming characteristics, but their charge carrier mobilities (ca. 0.1−0.3 cm^2/V•s) are highly dependent on the purity, regioregularity, deposition conditions, and molecular weight of the polymer.[3] On the other hand, oligomers such as α,α′-dihexyloligothiophenes are relatively facile to prepare and purify and exhibit appreciable mobilities when deposited by thermal evaporation in a vacuum (<1 cm^2/V•s).[4] However, the solubility of such linear oligothiophenes, even with solubilizing terminal alkyl chains, is still problematic for liquid-based device fabrication; hence, the number of fluidic assembled oligothiophene OFETs is relatively meager.[5]

We previously reported on the synthesis and properties of 2,5,2′,5′-tetra(4-*tert*-butylphenyl)-1,1′-biphenyl (**I**) as a prototype of an interesting family of oligophenyl-based swivel cruciforms.[6] The term swivel form relates to the fact that there is, at least in principle, free rotation between the arms in addition to within the arms. The single-crystal structure analysis and ^{1}H NMR spectrum of **I** revealed that the molecule adopts a folded structure, independent of the medium, as a consequence of strong intramolecular $\pi-\pi$ interaction. Such a molecular property led us to investigate if such a molecular design might be advantageous for solution-phase fabrication of ordered thin-film OFETs. In this Communication, we report on the synthesis and transistor properties of the new α,α′-dihexylpentathiophene-based swivel cruciform dimer depicted in Figure 1.

DHPT-SC was synthesized via a palladium-assisted Suzuki coupling as depicted in Scheme S1 (Supporting Information). Interestingly, this molecular shape seemed to enhance the solubility, which allowed for a detailed characterization of **DHPT-SC** by NMR spectroscopy. There is a slight downfield shift (~0.15 ppm) in the thienyl signals relative to those of other oligothienyls, which indicates that **DHPT-SC** also adopts a folded π-stacked conformation in solution. Differential scanning calorimetry (DSC) measurements of **DHPT-SC** showed only one distinct transition at 196 °C. During cooling, the isotropic−crystalline transition was observed at 178 °C. Such thermal behavior indicates the propensity of the molecule to form a reproducible crystalline phase, at least upon thermal treatment. A melting enthalpy value of 50.9 J/g was calculated from the integration of the melting curve, which is ca. 3 times larger than the melting enthalpy of high-molecular-weight poly(3-hexylthiophene).[7]



DHPT-SC

Figure 1. Structure of α,α′-dihexylpentathiophene-based swivel cruciform.

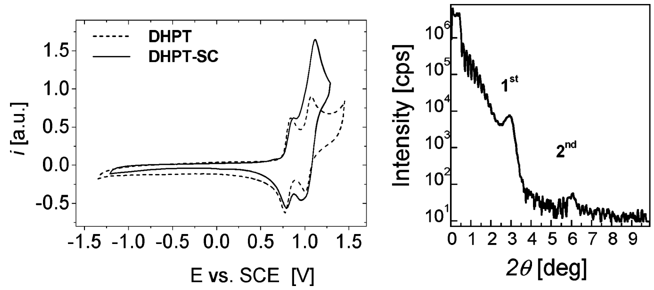


Figure 2. (Left) CV in $CH_2Cl_2/n\text{-}Bu_4NPF_6$, $\upsilon = 100$ mV/s. (Right) X-ray reflectivity pattern of the thin film of **DHPT-SC**.

We note only a minor shift between the dilute solution absorption spectrum of **DHPT-SC** and that of the linear α,α′-dihexylpentathiophene (**DHPT**) (Supporting Information). Conversely, there is a large red-shift (50 nm) in the PL maximum, which is most probably due to the formation of an intramolecular excimer in **DHPT-SC** upon photoexcitation. The cyclic voltammograms (CVs) of **DHPT-SC** and **DHPT** in $CH_2Cl_2/n\text{-}Bu_4NPF_6$ exhibited only a negligible difference in the first oxidation potentials and indicate that both molecules have similar ionization potentials (Figure 2, left). The CV and UV−vis data are in accord and imply that there is little electronic interaction between the arms in the ground state. The subsequent oxidation patterns at higher voltages differ slightly. However, this is not unexpected, as the presence of the two dihexylpentathiophene moieties in **DHPT-SC** implies that more than two electrons can be delivered within the applied potential range and also the oxidation to higher charged species is influenced by the neighboring arm.

As the goal of this work was to prepare OFETs using wet processes, we first investigated the structure of thin films formed from chloroform solutions using X-ray reflectometry. Figure 2

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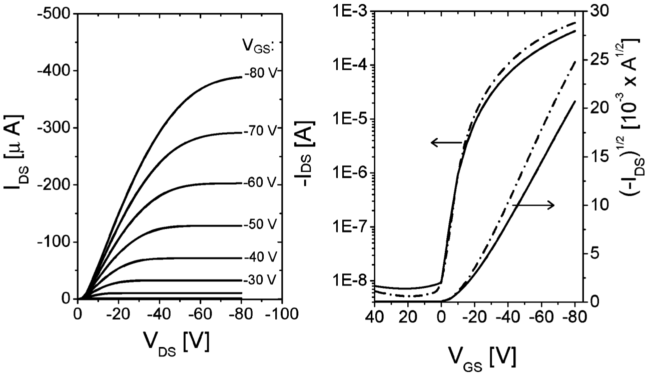

Figure 3. Characteristics of **DHPT-SC** OFET device for as-prepared (solid lines) and annealed sample (dashed−dotted lines). (Left) $I_{DS}-V$ plot at various gate voltages. (Right) Transfer and square root plot.

(right) shows the scattering pattern from a thin film that was annealed at 120 °C for 5 min, followed by slow cooling (1.3 K/min). Interestingly, the appearance of clearly resolved Bragg peaks (first- and second-order peaks of the interlayer distance) indicates that **DHPT-SC** forms a well-ordered layered structure in the solid state as typically observed for α,ω-dihexyloligothiophenes.[8] Using the Debye−Scherrer formalism, we calculated the domain size to be about 25 nm. The *d*-spacing is ca. 3 nm, consistent with an almost upright orientation of the pentathiophene units, despite the covalent linkage between the arms. Kiessig thickness fringes are clearly visible up to the first diffraction peak (1st), indicating that **DHPT-SC** forms smooth layers of a thickness of 52 nm.

OFETs with bottom contact geometry were fabricated on highly doped n-type silicon wafers, and the organic semiconductor layers (ca. 50 nm) were deposited from chloroform solutions. Since previous studies on poly(3-hexylthiophene) revealed that thermal treatment of the thin films prior to the deposition of the source and drain electrodes improved the OFET performance,[9] we also examined the transistor properties of **DHPT-SC** after the annealing conditions described above. All preparation processes and characterization of the devices were performed inside a nitrogen atmosphere glovebox, and the charge carrier mobilities were calculated using the OFET equation.[10]

The output characteristics from OFETs based on as-prepared **DHPT-SC** are shown in Figure 3, left. The OFETs exhibited negative amplification, which is typical of p-type semiconductors with well-defined linear and saturation regions. No hysteresis was observed in the measurements, which indicates very good current modulation and stability during operation. For nonannealed **DHPT-SC**, we obtained a field-effect mobility (μ_{FET}) of 9.6×10^{-3} cm^2/V•s and a current on/off ratio of 6×10^4 at $V_{DS} = -80$ V (Figure 3, right). The device made from the annealed sample gave a slight improvement in charge carrier mobility ($\mu_{FET} = 0.012$ cm^2/V•s), with an increased on/off ratio ($>10^5$). Additionally, the turn-on voltages ($V_o \approx 0$V) are very small for both devices, which is a highly desirable OFET property as such transistors have low power consumption.

In conclusion, we have prepared a novel pentathiophene-based swivel cruciform **DHPT-SC**. The material exhibits a weak, noncovalent interaction between the arms in solution, and coupled with the increased solubility of the dimer, this allows for the fluidic preparation of homogeneous microcrystalline films. OFETs based on **DHPT-SC** exhibited high field-effect mobility up to 0.012 cm^2/V•s, which is one of the highest values reported to date for wet-processed OFETs utilizing oligothiophenes.[1f] Further modifications to the structure and an in-depth examination of the morphological and optical characteristics are underway, which should allow a better understanding of the structure−property relationship.

Supporting Information Available: Details of experimental procedures, spectroscopic data, and device fabrication. This material is available free of charge via the Internet at http://pubs.acs.org.

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