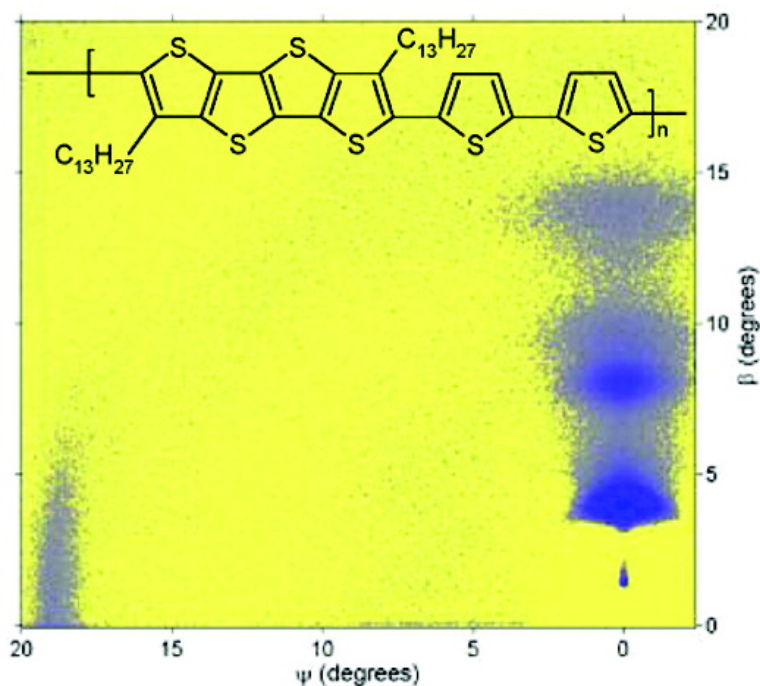


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Tetrathienoacene Copolymers As High Mobility, Soluble Organic Semiconductors

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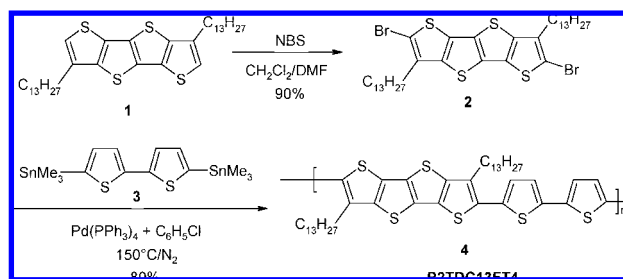
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The development of polymer thin film transistors is viewed as a critical enabling step for the realization of large-area, mechanically flexible electronics.^{1,2} Extensive studies have been carried out on soluble thiophene polymers, in which a semiconducting thiophene backbone is functionalized with alkane side groups to enhance solubility. Regioregular poly(3-hexylthiophene) (P3HT) has emerged as the benchmark for this class of materials.^{1,3} The regioregularity of the alkyl chains allows the chains to pack more efficiently in the solid-state compared to their regiorandom analogues, leading to field-effect hole mobilities up to 0.1 cm²/V·s.¹ However, regioregularity also leads to longer effective conjugation lengths and P3HT can be easily oxidized in air because of its low ionization potential and can undergo photoinduced oxidation due to its small HOMO–LUMO band gap.⁴

Attempts to engineer higher performance polythiophenes (other than copolymerization with different units⁵) focus on improving chain packing in the solid state and widening the band gap.^{6,7} The former is viewed as the way toward higher mobility while the latter, together with the associated increase in the ionization potential, leads to better (photo)oxidative stability. One strategy involves the reduction of the number of alkyl substitutions on the thiophene backbone, as in poly(3,3''-dialkyl-quarterthiophene)s (PQTs).^{9,10} The unsubstituted bithiophenes have enough rotational freedom to reduce the effective conjugation length with respect to the fully substituted analogues thereby yielding a wider band gap. Moreover, the resulting increase in free volume was found to promote self-assembly and crystallization. As a result, field-effect hole mobilities up to 0.2 cm²/V·s were observed after postdeposition annealing.⁸ A second strategy involves the introduction of an unsubstituted unit that consists of two fused thiophene rings as in poly(2,5-bis(alkylthiophen-2-yl)thieno[3,2-b]thiophenes) (pBTTT).^{11–15} The rotational invariance of the fused unit promotes the formation of highly crystalline regimes. As a result, the chains can assemble into large crystalline domains on crystallization from a liquid crystal phase, and field-effect hole mobilities of 0.2–0.6 cm²/V·s were observed.^{11,13–15} (A recent detailed study of contact effects places the field-effect mobility at 1 cm²/V·s,¹⁶ indicating that systematic optimization on device level is needed to reach the ultimate mobilities in these materials.) Moreover, the fused unit was found to cause a reduction in electron delocalization over the polymer backbone, widening the band gap with respect to regioregular poly(3-alkylthiophene)s.

In this Communication we demonstrate that high performance, soluble polymeric semiconductors can be achieved by increasing the rigidity of the thiophene monomer through the use of an alkyl-substituted core that consists of four fused thiophene rings. We

Scheme 1. Synthetic Scheme for P2TDC13FT4



report on a member of the family of dialkylated tetrathienoacene copolymers, namely poly(2,5-bis(thiophene-2-yl)-(3,7-ditri-decyl)tetrathienoacene) (P2TDC13FT4), that can be deposited from solution into highly ordered films with a field-effect hole mobility exceeding 0.3 cm²/V·s.

Increasing the rigidity in organic semiconductors is known to lead to better stacking and better charge transport properties. A textbook example is pentacene, a molecule that consists of five fused benzene rings, and exhibits a remarkable field-effect hole mobility exceeding 1 cm²/V·s¹⁷ as a consequence of its strong tendency to crystallize.¹⁸ However, increasing rigidity in thiophenes is known to decrease solubility and environmental stability. We have recently developed a family of β -alkylsubstituted fused thiophene compounds that successfully addresses these two issues.¹⁹ Alkyl substituents in the β positions render the molecules soluble, yet the α positions are left available for polymerization. At the same time, fused thiophene compounds are known for their very good environmental stability owing to their relatively large band gaps.^{20,21} Copolymerization of these compounds with a bithiophene moiety (Scheme 1) led to a novel family of polymeric semiconductors. From design point of view this family of materials has the potential to lead to good polymer backbone π – π stacking combined with good solubility and stability.

The synthesis of P2TDC13FT4 is illustrated in Scheme 1. The detailed procedure can be found in the Supporting Information. The optical absorption spectrum of P2TDC13FT4 films shows a $\lambda_{\text{max}} = 546$ nm that suggests a similar band gap as the two-fused-ring system pBTTT (with $\lambda_{\text{max}} = 547$ nm).¹¹ Differential scanning calorimetry shows no melting and no phase transitions up to 350 °C. This is a major difference with pBTTT—the latter shows a liquid crystal phase and achieves its high mobility when carefully cooled from it.^{11,13,14}

Despite the lack of a liquid crystalline transition, P2TDC13FT4 yields highly ordered films. Films were prepared by spin coating from a room temperature, 3 mg/mL 1,2-dichlorobenzene solution (the solution had been briefly heated to 150 °C to speed up dissolution). A grazing incidence wide angle synchrotron X-ray

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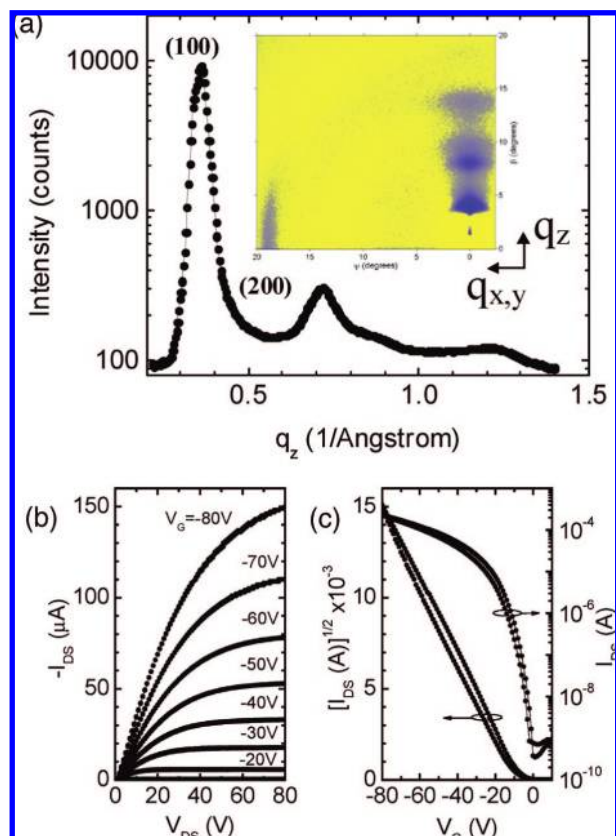


Figure 1. (a) Grazing incidence X-ray scattering map (inset) and analysis of the in-plane data from a P2TDC13FT4 film deposited on HMDS treated silicon oxide; (b) output and (c) transfer characteristics from a top contact, bottom-gate P2TDC13FT4 transistor for $V_{DS} = -80$ V.

scattering map from a P2TDC13FT4 film deposited on an oxidized silicon wafer treated with HMDS is shown in the insert of Figure 1a. The data are consistent with the formation of conjugated lamellae parallel to the substrate, as observed in several regioregular polythiophenes.¹ Evaluation of the out-of-plane data (q_z) reveals a lamellar spacing of 17.5 Å. Analysis of the in-plane peak (q_{xy}) reveals a spacing of 3.76 Å, which is usually assigned to π - π stacking in polythiophenes. This spacing, which is an important parameter for charge transport, is comparable to what is observed in PQT (3.8 Å)⁸ and pBTTT (3.7 Å)¹¹ after careful postdeposition annealing treatments.

Figure 1b shows the output characteristics of a P2TDC13FT4 transistor with Au top contacts fabricated on an oxidized silicon wafer treated with HMDS. Details are included in the Supporting Information. The linearity of the curves in the low V_{DS} regime (0 to -5 V) indicates that Au forms an ohmic contact with P2TDC13FT4. The parasitic resistance of the contacts, evaluated with the transmission line method²² using channel lengths from 50 to 150 μm , was found to be in the range from 7 to 40 $k\Omega \cdot cm$, a value comparable to that in high mobility pentacene transistors.²² The transfer characteristics in Figure 1c reveal a field-effect hole mobility of 0.33 $cm^2/V \cdot s$, an on/off ratio exceeding 10^5 , and a threshold voltage of -10 V.

It should be noted that devices fabricated in a glovebox and measured under vacuum yielded the same output characteristics as devices fabricated and tested in ambient. Moreover, a device with

an octyltrichlorosilane-modified gate dielectric showed no significant degradation in its output characteristics over 9 months when stored at 30% relative humidity. These observations point to the excellent environmental stability of P2TDC13FT4. It should also be noted that the P2TDC13FT4 films were dried at 80 or 150 °C to remove the remaining solvent. Drying temperature and cooling rate did not seem to affect device performance, meaning that there is no need for complex postdeposition processing.

In conclusion, we show that dialkylated tetrathienoacene copolymers represent a new class of organic semiconductors that can be easily processed from solution into ordered, high mobility thin films. Their chief advantages are their environmental stability and their straightforward solution processing which make them particularly attractive for applications in large-area, mechanically flexible electronics.

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Supporting Information Available: Synthetic, experimental procedures; device characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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