Tetrathiahexacene as Building Block for Solution-Processable Semiconducting Polymers: Exploring the Monomer Size Limit

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The search for organic semiconductors suitable to produce flexible, lightweight, and cost-effective devices is the focus of many research groups around the globe.^{1,2} There is a particular interest in organic field-effect transistors which may be used in various applications such as RFID tags.^{3,4} Great advances have been achieved, pushing upfield-effect mobilities almost to the regime of amorphous silicon.^{5–7} Especially thiophene-containing polymers are highly promising toward applications due to their good mobility obtained by simple solution-based processing techniques.^{8,9} Poly(3-hexylthiophene) (**P3HT**) is among the most intensively studied semiconducting polymers.^{10–12} However, it does not meet all requirements for device production such as, for instance, operational stability under ambient conditions.¹³

To improve the properties of **P3HT**, comonomers consisting of fused polycycles have been introduced into the polythiophene chain. Benzodithiophene (**P1**), for example, increases the ionization potential of the resulting polymer, thus also increasing its stability.^{14,15} In addition, the structural order of the polymer in the film is enhanced by the high aggregation tendency of the large monomer. Fused oligothiophenes have also been used, such as dithienothiophene (**P2**), with remarkable stability and high charge-carrier mobility.¹⁶ The largest building block in a soluble polythiophene so far is tetrathienoacene (**P3**).¹⁷ This polymer is very stable toward oxidation in an organic field-effect transistor and also shows high charge-carrier mobilities.

The aim of the present work is to show whether an even larger fused monomer in a polythiophene chain can further improve stability and device performance. The crucial point is the question if a sufficiently soluble polymer can be obtained yielding highly ordered films upon processing. Tetrathiahexacene (2) was chosen as building block to extend the monomer size beyond the current limit. It allows the attachment of alkyl chains in a way that no steric repulsion between neighboring chains disturbs the packing and that the polymer can benefit from the high aggregation tendency of extended polycyclic aromatic hydrocarbons.^{18,19}

The synthesis is outlined in Scheme 2. It starts with routine thiophene chemistry: bromination of 3-iodothiophene (1), selective Sonogashira coupling with tetradecyne, and Stille coupling with bis(trimethylstannyl)thieno[2,1-b]thiophene (4), which is made according to the literature procedure.²⁰ The key step to make the desired molecule is a base-induced cyclization of two triple bonds of the thieno[2,1-b]thiophene core in molecule 5, forming benzene rings with attached alkyl chains. When using the strong nonionic base diazabicycloundecene



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Figure 1. UV-vis absorption spectra of **PTTH** in *o*-dichlorobenzene at a concentration of 10^{-4} M with regard to the repeat unit. Extinction coefficients are calculated for the repeat unit of the polymer.

(DBU) in N-methylpyrrolidone (NMP), the target molecule 6 can be obtained in high yield. An initial attempt to form a polymer out of this building block targeted a homopolymer. For this reason, structure 6 was brominated with NBS to allow a nickel-catalyzed dehalogenation polymerization. However, no soluble polymer was obtained. The polymer chain is obviously too stiff to be solubilized by the alkyl chains. To increase the solubility, additional dithiophenes have been introduced to yield poly(tetrathiahexacene-alt-ditetradecyldithiophene) (PTTH). This goal is reached by a Stille copolymerization. Compound 6 was doubly lithiated by tert-butyllithium and subsequently treated with trimethyltin chloride, yielding the bis-stannylated compound 7. The polymerization using dibromodithiophene (8) as comonomer was performed using $Pd(PPh_3)_4$ as catalyst in toluene. The reaction mixture was heated for 40 min in the microwave to 150 °C with a power density of 70 W/mL. The product which precipitated in the reaction medium could be dissolved in dichlorobenzene. After reprecipitation and Soxhlet extraction to remove low molecular weight material, the pure polymer was obtained with a molecular weight of $M_{\rm n} = 18$ kg/ mol and $M_{\rm w} = 42$ kg/mol as determined by size-exclusion chromatography in reference to polystyrene as standard. The latter value corresponds to a degree of polymerization DP = 32. It is known from other polymers that the charge-carrier mobiity drops with very low molecular weights, but the value reached for **PTTH** should be sufficient to explore the device performance.^{21,22}

The UV-vis absorption spectrum of **PTTH** (Figure 1) in a dichlorobenzene solution shows three resolved bands around 500 nm at room temperature. The spectrum almost resembles the absorption of the film which means that the chains are close to each other in solution similar to the situation prevailing in the film, indicating high intermolecular forces of the fused system in solution. When the polymer solution is heated to about 100 °C, the bands at 520 and 560 nm vanish. Only one broad peak at 450 nm remains, which is typical for polythiophenes like **P3HT** and structurally related polymers with a tendency to aggregate in solution.^{23,24} At elevated temperatures, the thermal motion reduces the aggregation and the absorption of a singly solvated polymer chain is detected.

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Scheme 2. Synthesis of PTTH^a



^a Conditions: (i) NBS, DMF, 1 h, 95%; (ii) 1-tetradecyne, Pd(PPh₃)₄, CuI, triethylamine, THF, RT, overnight, 98%; (iii) Pd₂(dba)₃, P(o-tol)₃, o-dichlorobenzene, 120 °C, 3 h, 64%; (iv) DBU, NMP, reflux, 78%; (v) 1: *tert*-butyllithium, THF, 0 °C; 2: Me₃SnCl, 42%; (vi) Pd(PPh₃)₄, toluene, MW, 150 °C, 80%.

The absorption onset at 550 nm is at about the same value as for **P3HT**. This means that **PTTH** possesses almost the same effective conjugation length despite the much stiffer polymer backbone. For **P3HT**, about 15 thiophene units have been determined at room temperature to constitute the effective conjugation length.^{25,26} Given a similar conjugation within and between the repeat units in both systems, this translates into less than two repeating units for **PTTH**, an amazingly low value.

To investigate the bulk morpholgy of the polymer, fibers have been extruded to measure two-dimensional wide-angle X-ray scattering. The diffraction pattern is shown in Figure 2. The well-resolved peaks indicate a pronounced ordering of the polymer. The equatorial reflections reveal lamellar order as typically observed for polythiophenes.

The lamellar distance was determined as 2.38 nm, which is about the length of the attached tetradecyl chain plus a thiophene unit. It is thus very likely that the alkyl chains of adjacent polymer chains interdigitate as depicted in Figure 2b. This explains the high order of the polymer in the bulk in addition to the aggregation of the large π -system. The latter is reflected by the very low $\pi - \pi$ distance (0.37 nm) as determined by the position of the equatorial reflections of the diffraction pattern. This value is as small as for other polymers showing field-effect mobilities well above $0.1 \text{ cm}^2/(\text{V s})$. A low stacking distance is important for high charge-carrier mobilities to reduce the potential barrier of a charge-carrier hopping from one chain to the neighboring one.²⁷

The polymer **PTTH** has been tested in a field-effect transistor using a silicon substrate which has been treated with HMDS to avoid charge-carrier trapping due to the acidic silicon dioxide dielectric surface. The polymer was spin-cast on top from a dichlorobenzene solution and annealed for 5 min at 100 °C.



Figure 2. (a) Two-dimensional wide-angle X-ray diffraction pattern of an extruded fiber of **PTTH**. (b) Cartoon suggesting the packing of the polymer. The polymer structures are obtained by an MMFF optimization and fit to the X-ray diffraction data.



Figure 3. Transistor characteristics of **PTTH** on a hexamethyldisilazane (HMDS)-treated silicon waver with top-contact gold electrodes: (a) transfer curve; (b) output curves.

Gold electrodes were evaporated on top. The measured curves can be seen in Figure 3. The average field-effect mobility extracted from the saturation regime was determined to be $(1.3 \pm 0.2) \times 10^{-3} \text{ cm}^2/(\text{V s})$ with an on-off ratio of 3.8×10^3 . This value does not reach a level required for applications, i.e., $0.1 \text{ cm}^2/(\text{V s})$, but with more processing optimizations such as using a top-gate transistor setup, this value may be accessible. It is well-known for **P3HT** that under standard testing conditions values exceeding $10^{-2} \text{ cm}^2/(\text{V s})$ are rarely measured, but under optimum conditions, much higher values can be reached.^{28,29} The transistor curves of Figure 3 demonstrate the high potential of the present material as the device shows very little hysteresis and no bias stress effects under the applied extreme conditions, i.e., the high potentials, as well as good reproducibility.

These parameters are known to be very important for reliable applications.³⁰

In summary, it could be demonstrated that a monomer consisting of six fused rings can still form a soluble polymer when copolymerized with alkylated dithiophenes. The strong interchain aggregation leads to highly ordered bulk material with low $\pi - \pi$ distance, showing the effectivity of introducing monomers of this size. In a field-effect transistor, good device characteristics, i.e., low contact resistance and low hysteresis, have been measured. The field-effect mobility does not yet reach values needed for applications but is likely to be achieved after more processing optimizations. The present results strongly support the potential of conjugated polymers containing large fused π -systems.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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