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5,6,11,12-Tetrachlorotetracene, a tetracene derivative with π-stacking structure: The synthesis, crystal structure and transistor properties

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Abstract

An important parameter for applications of organic semiconductor in devices is their charge-carrier mobility. It has been predicted theoretically that forming face-to-face π-stacks at the molecular level may increase the charge-carrier mobility due to enhanced electronic couplings. To achieve different molecular arrangements, we recently synthesized and crystallized a tetracene derivative, 5,6,11,12-tetrachlorotetracene. The X-ray crystal structure shows that the molecules form slip π-stacks in contrast to herringbone type tetracene. Comparison of electrostatic potential maps of tetrachlorotetracene and the parent tetracene molecule shows that the slip-stack packing structure is favored in terms of electrostatic forces due to the substituents in tetrachlorotetracene crystals. Single crystal field-effect transistors based on tetrachlorotetracene crystals show p-type behavior with a field-effect mobility of 1.7 cm^2/V s, which is among the best values reported for organic field-effect transistors. These results, together with several recent findings, may serve as guidance in search of new organic semiconductors with high performance.
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1. Introduction

One of the key physical parameters for successful use of organic semiconductor devices is the charge-carrier mobility, i.e. the efficiency of charge transport. The effective mobility of a transistor device can be improved by optimizing a number of factors including the purity and structural quality of the active organic layer, the quality of the dielectric layer, the interfaces between the different layers, and in the case of thin-film devices, film morphology, etc. [1,2].

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An alternative way to increase the intrinsic charge-carrier mobility is to design new molecular materials with high intrinsic mobility, and the recent development of organic single crystal field-effect transistors (FETs) provides a convenient method for measuring the mobilities in organic materials [3]. Theoretically, high mobility can be achieved through strong intermolecular electronic coupling [4–8], and for planar carbon-based organic molecules, the intermolecular electronic coupling may be maximized in a face-to-face stack of the π-electron systems (π-stack) [4,6]. For instance, rubrene (I) may be considered such a molecule with a crystal structure showing a slip-stack arrangement [9]. Within each stack, the rubrene molecules are displaced along the long axis of the tetracene backbone, while there is virtually no displacement along the short axis (perpendicular to the long axis), resulting in an overlap of approximately 60% of the tetracene backbone (π-electron systems) with adjacent molecules. In comparison, unsubstituted tetracene or pentacene adopt herringbone-type packing arrangements [10] with an edge-to-face pattern, and thus the π–π overlap is not maximized. Single crystal rubrene field-effect transistors revealed anisotropic charge-carrier mobilities, with the highest reported value of approximately 20 cm^2/V s in the stacking direction [11], consistent with quantum chemical calculations of the anisotropic transfer integrals [9]. Despite the recent progress on new materials with π-stack patterns [12–16], experimental evidence that such structures can have higher mobilities than herringbone-packed solids is still scant [6]. One of the problems is the lack of suitable molecules for the study. It is therefore necessary to synthesize novel molecules that form π-stack arrangements and to study their electronic transport properties. The results may then serve as guidance in search of high performance organic semiconductors.
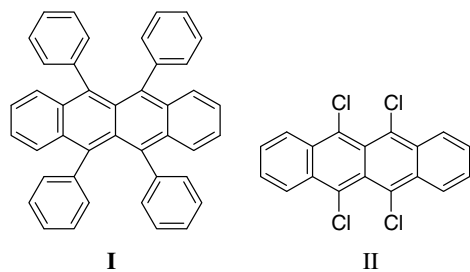
I   **II**

We recently synthesized and crystallized a tetracene derivative, 5,6,11,12-tetrachlorotetracene (II). The synthetic procedure was established 30 years ago [17], but the crystal structure and the transport properties were never reported. In this paper, we describe the crystal structure and FET properties based on this material. In particular, we show that the molecule crystallizes in a slip-stack pattern with a high mobility along the stacking direction, and we further performed quantum mechanical calculations to investigate the origin of the slip-stack arrangements of this tetracene derivative.

2. Experimental section

The synthesis of II followed a previously published procedure [17] with the synthetic Scheme 1 shown below. Refluxing a mixture of 6,11-dihydroxy-5,12-naphthacenedione (Aldrich) and PCl$_5$ in POCl$_3$ affords hexachloro intermediate in 53% yield, which is then refluxed with NaI in DMF giving molecule II in 73.4% yield. The crude product can be recrystallized from acetic acid to give red transparent needles.

Single crystals for both X-ray and electronic transport measurements were subsequently grown by horizontal physical vapor phase transport in a stream of high purity argon using a modified apparatus previously described by Laudise et al. [18]. Here, two glass tubes of different diameters were used, with the outer tube wrapped with two rope-heaters defining source zone and crystal growth zone, respectively. A glass tube of smaller diameter served as the sample container. The source temperature was held at 215 °C, and the argon flow rate was 19 ml/min. Typical needle-like crystals showed dimensions of 1–8 mm in length, 0.1–0.5 mm in width, and 0.05–0.1 mm in thickness.

The crystals were analyzed using an Oxford-Diffraction Xcalibur2 CCD X-ray diffractometer, using graphite monochromated MoKα radiation. CCDC 634428 contains the supplementary crystallographic data for this paper [19].

The charge transport properties were measured using field-effect transistors fabricated on single crystals [3]. The needle-like habit of the crystals allowed measuring the charge transport along the a-axis, and therefore, along the π-stacks. We used graphite ink to paint source and drain electrodes while a Parylene-N film served as gate dielectric [20–23]. The gate material was again graphite ink. Parylene-N was deposited on top of the crystal in a home-made reactor, and its thickness was determined with a profilometer. The channel capacitance was then calculated from the measured thickness and the tabulated dielectric constant of Parylene
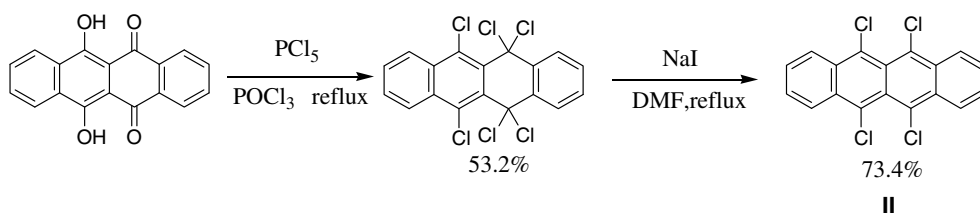
Scheme 1. Synthesis of tetrachlorotetracene (II).

N ($\varepsilon = 2.65$). Typical FET dimensions of the channel lengths (l) and widths (w) were 0.5 mm 0.3 mm, respectively. The FET characteristics were measured using a probe station and a HP 4155A semiconductor parameter analyzer.

Quantum chemical calculations were carried out using the Spartan 04 program. All calculations were performed using B3LYP hybrid density functional theory at the $6-31 + G^*$ level, including the geometry optimization, the HOMO energy level and the electrostatic potential (ESP) maps.

3. Results and discussion

3.1. X-Ray crystal structure

Tetrachlorotetracene crystallizes in a monoclinic unit cell with space group symmetry $P2_1/n$. Fig. 1a and b show the molecular structure of a single molecule in different orientation while the molecular packing is shown in Fig. 2. The four benzene rings of the tetracene backbone are not quite coplanar but adopt a "Z" shape (Fig. 1b). The two pairs of

chlorine atoms point in the opposite directions: one pair attaching to the same benzene ring (left to the center) points upwards while the other pair of the neighboring benzene ring (right to the center) points downwards. The dihedral angle of the carbon–chlorine bonds in each side of the molecule is about 33°. The molecules form isolated stacks along the a-axis, with an inter-planar distance of 3.58 Å (Fig. 3), slightly larger than the sum of the van der Waals radii. Fig. 3 is a projection diagram depicting the overlap between two neighboring molecules within a stack. There are slight shifts along both the long and short molecular axes (of the tetracene backbone), with a displacement of 0.6 Å and 1 Å along short and long molecular axis, respectively; the latter is much shorter than the value found in rubrene (6.1 Å). These shifts make it possible for eight pairs of carbon atoms to be superimposed between two neighboring molecules (Fig. 3). The stacks are isolated, with no π–π interaction between them, and the closest carbon–carbon distance is found to be 3.83 Å. Thus, the crystal structure indicates that this molecule forms a one-dimensional crystal with strongest interaction along the a-axis, consistent with the needle-like habit of the red crystals.

3.2. Computational studies

The calculated bond lengths and bond angles are all in good agreement with the single crystal structure data, with the largest difference in bond lengths being 0.014 Å (~1%). The predicted structure reproduces the "Z" shape (Fig. 4) and the orientation of the two pairs of chlorine atoms. The dihedral angle of the carbon–chlorine bonds on each side of the molecule is 35° compared to 33° found in the crystal structure (Fig. 1b). Thus, the observed crystal/molecular structure matches well with the calculated structure of the tetrachlorotetracene molecule in the gas phase. The solid-state packing has therefore little effect on the molecular conformation (structure) in the crystal.
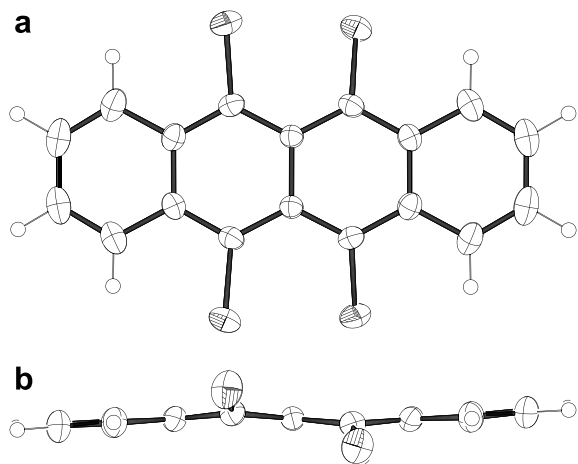

Fig. 1. X-ray crystal structure of tetrachlorotetracene (a) view perpendicular to the molecular plane (b) side view of tetrachlorotetracene showing non-planarity of the molecule.
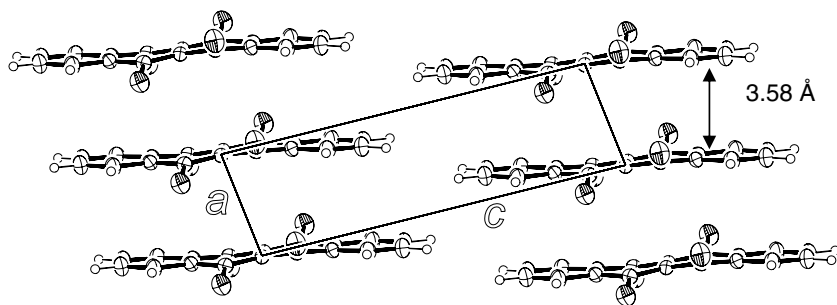
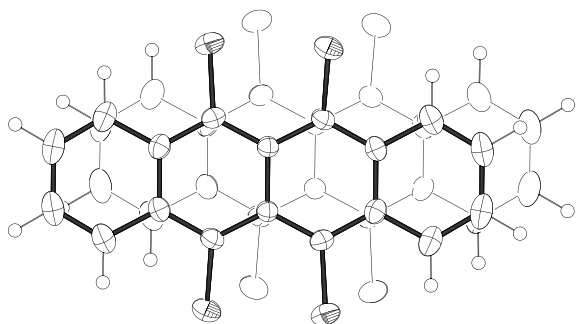Fig. 2. The stacking pattern of tetrachlorotetracene along a axis.

Fig. 3. Projection diagram of two neighboring molecules within a stack. Black thick lines are used to identify the molecule on the top while thin lines are used for the molecule below it.
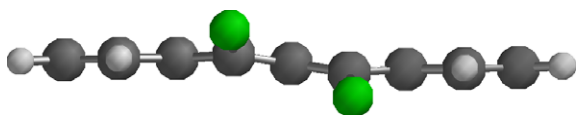

Fig. 4. Calculated structure of tetrachlorotetracene.

The calculated HOMO energy level of tetrachlorotetracene is 0.52 eV lower than that of the parent tetracene molecule, indicating that the addition of chlorine atoms to the parent tetracene should increase the stability of the system towards oxidation. This is consistent with our observation that a solution of tetracene loses its orange color rapidly, while tetrachlorotetracene can be recrystallized from several organic solvents without protection. Both enhanced solubility and stability found in this material are important parameters for large-area applications where inexpensive fabrication methods such as solution processing are desired.

A simple model proposed by Hunter and Sanders [24] suggests that an aromatic system can be pictured as a positively charged σ-framework sandwiched between two negatively charged π-electron clouds, and that the net favorable π–π interactions

between molecules are actually the result of π-σ attractions that overcome π–π repulsions. Therefore, the electrostatic force rather than the π–π overlap controls the geometry of molecules in a crystals [24]. Electrostatic interactions can be qualitatively predicted by drawing electrostatic potential (ESP) maps, which were recently used to explain the slipstack arrangements observed in several fluorinated thiophene and selenophene-based polymers [25]. Such ESP maps combine electrostatic potential and electron density surfaces, and thus convey which regions of a molecule are electron rich (indicated in red) and which are electron poor (indicated in blue), as shown in Fig. 5 for both tetracene and tetrachlorotetracene.

In the parent tetracene molecule (Fig. 5a), the π electrons have the highest probability to be found above (and below) the four aromatic rings (red), while the edge of the molecule (where the hydrogen atoms are located) is electron-deficient (blue). One can imagine that stacking of tetracene molecules is energetically unfavorable due to the repulsive force of the π-electrons, but would otherwise provide an efficient overlap. Therefore, polyacenes, including tetracene and pentacene, adopt a herringbone structure instead of face-to-face stacks. In contrast, for tetrachlorotetracene (Fig. 5b), the electron density on the surface of the tetracene backbone is significantly reduced and the electron rich regions only exist at the two ends (red) of the ring system. This redistribution of the π electrons may favor a slip-stack arrangement so that the electron rich region is paired with the electron poor region, while maintaining optimal space filling. Also notice that the locations of carbon atoms bear the highest electron densities while the centers of the benzene rings are electron-deficient (Fig. 5b). This may explain the slip-stack overlap geometry illustrated in Fig. 3, where the centers of the benzene rings of one
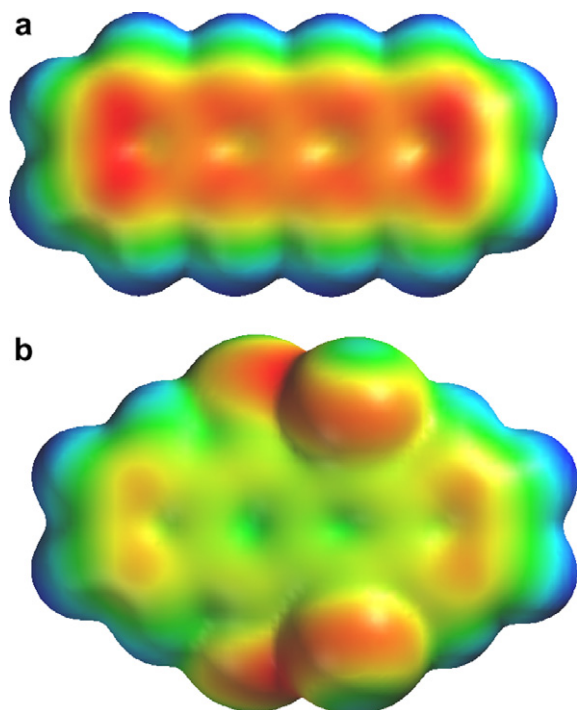
Fig. 5. ESP surface plots for (a) tetracene (b) and tetrachlorotetracene.

molecule are almost superimposed on the carbon atoms of the other molecule, thus optimizing the electrostatic forces between the stacked molecules.

3.3. Single crystal field-effect transistor

Typical output and transfer characteristics of single crystal FET transistors at room temperature are shown in Figs. 6 and 7, respectively. The negative gate bias required indicates that holes are the charge-carriers (p-type semiconductor). At low drain–source voltage V_{ds}, the drain current exhibits a nonlinear dependence on V_{ds}, suggesting non-Ohmic contact behavior. At higher voltages, however, saturation is observed as V_{ds} becomes comparable to V_{gs}, indicating that the contact resistance does not dominate the transconductance in this region. From the transfer characteristics in Fig. 7 we extracted an on/off current ratio of $\sim 10^4$, a field-effect mobility of 1.7 cm^2/V s, and a threshold voltage of $V_t \sim -12$ V. The fairly large threshold voltage indicates a large trap density, which could be a significant factor in reducing the FET-mobility. Therefore, the intrinsic p-type mobility in tetrachlorotetracene single crystal is likely to be higher than 1.7 cm^2/V s. Occasionally, a field-effect mobility as high as 5 cm^2/V s was observed, but was not clearly reproducible.

A number of techniques have been used to measure the charge-carrier mobility in organic single crystals [3], and in some cases different results for the same material have been reported [26]. Furthermore, the chemical purity and quality of the crystal also affect the observed mobility [27]. However,
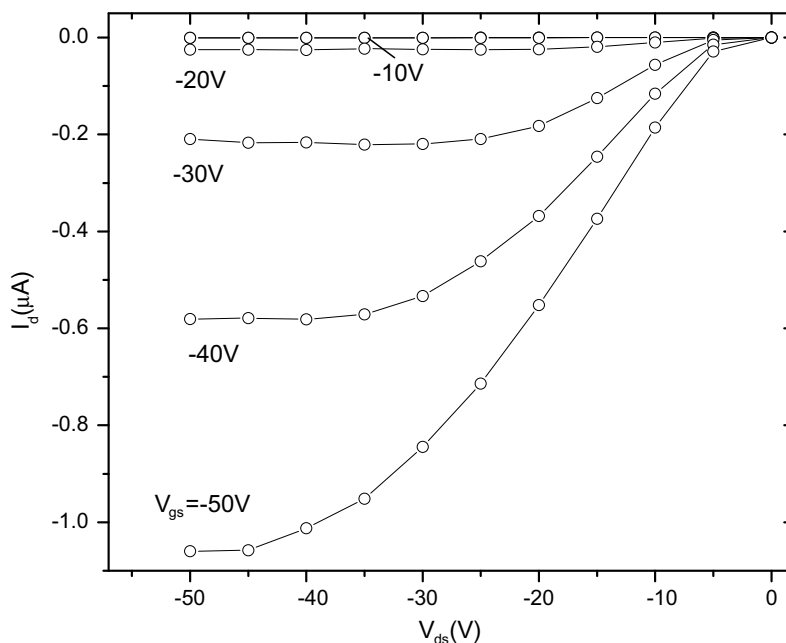

Fig. 6. Output characteristics of a typical tetrachlorotetracene single crystal field-effect transistor.
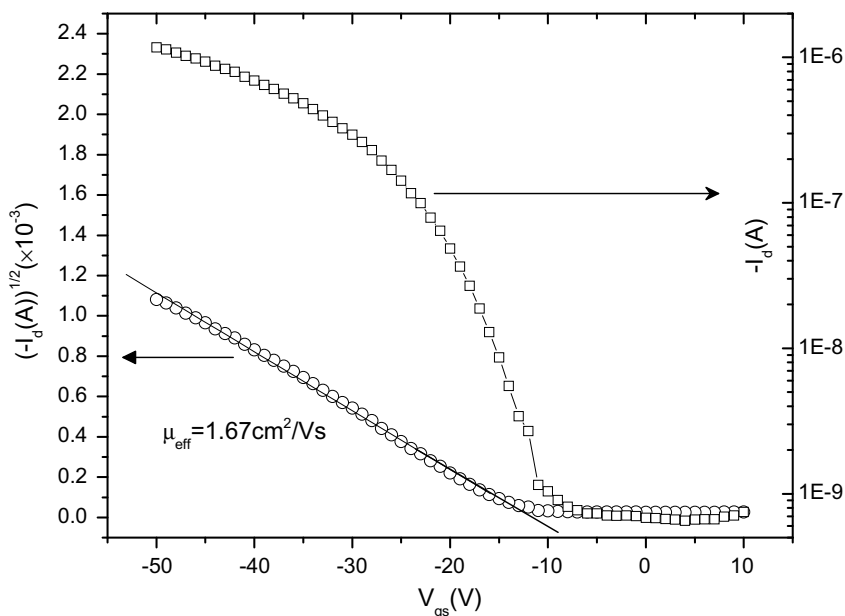
Fig. 7. Transfer characteristics of a typical tetrachlorotetracene single crystal field-effect transistor.

among three types of tetracene derivatives we have measured using the same technique, (parent) tetracene, tetrachlorotetracene (title compound) and tetraphenyltetracene (rubrene), both rubrene and the tetrachlorotetracene crystals showed significantly higher mobility than parent tetracene crystal [28]. Note that both tetrachlorotetracene and rubrene adopt slip-stack pattern whereas in parent tetracene crystal there is little π–π overlap between parallel molecules. Furthermore, the tetrachlorotetracene used in this study was purified only once before crystallization from the gas phase. Therefore, our results provide further evidence that π-stacking allows efficient charge-carrier transport along a stack and that molecules crystallizing in stack patterns promise high charge-carrier mobility, consistent with a recent report [14]. Although we have not yet performed thin-film transistor measurement on the title compound, the present results already give important information in designing new organic semiconductors with high charge-carrier mobility. Furthermore, the results indicate that for thin-film transistors, high mobility can be achieved when the molecules stack at the gate–semiconductor interface along the channel direction.

4. Conclusion

The tetracene derivative, 5,6,11,12-tetrachlorotetracene, crystallizes in isolated slip-stacks with enhanced π–π overlap within the stacks, but little interactions between them. ESP surface maps show that the slip-stack arrangement is favored by the modification of electrostatic potential surface of the tetracene backbone due to the chlorine atoms compared to the parent tetracene molecule (herringbone). A hole mobility in single crystal FETs as high as 1.7 cm^2/V s was achieved along the stack direction. Our next step is to test and optimize thin-film transistor of the title compound, and to synthesize other molecules with stacking patterns to move towards the high mobility limit in organic semiconductors.

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[28] Using the same techniques we measured transistor properties of single crystals of tetracene and rubrene. The results vary with the purity and crystal qualities. The highest mobility we obtained for rubrene and tetracene were $15 \, cm^2/V \, s$ and $1.0 \, cm^2/V \, s$, respectively.